



# CHEMICAL ABSTRACTS

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## I—APPARATUS

C. G. DERICE

Report on the calibration of sixteen Lovibond red glasses of nominal value 7.6. I. G. PRIGER. *Cotton Oil Press* 4, No. 9, 43-4(1921).—At the urgent request of the Color Committee of Am. Oil Chem. Soc. the U. S. Bur. of Standards calibrated 16 Lovibond red glasses of nominal value 7.6 for members of the Soc. The Lovibond equivalent of each of the glasses was detd. in terms of the red set B. S. No. 9940 used in connection with 35.0 yellow B. S. glass 10289 B. by means of the Arons chromoscope. The av. of the 16 is 7.7 red, i. e., 0.1 lighter than their nominal value; 1 is 0.54 darker than 7.5, the others all varying less than 0.33 from this figure. A study was also made of the precision and reliability of Lovibond grading at about 35.0 y, 7.6 r and it was noted that (1) the av. deviation of a single observation from the mean is about 0.1; (2) the max deviation of a single observation from the mean is as much as 0.4; (3) the a. m. and p. m. means differ from the mean by 0.1 in some cases; and (4) the pretended accuracy of grading to 0.1 r at this point on the color scale is entirely illusory.

H. S. BAILEY

Notes regarding the construction of platinum resistance thermometers and immersion heating coils of low lag. T. S. SLIGH, JR. *J. Am. Chem. Soc.* 43, 470-5 (1921).—The flat calorimetric resistance thermometers of the Dickinson-Mueller type have generally shown strain, indicated by a low value (about 1.47, sometimes 1.4, instead of 1.495 for unstrained wire) for the  $\delta$  of the Callendar formula. "Flash"-annealing, or sudden heating of the wire to 1000°, without dehydrating the mica core, relieves strain in the completed thermometers. A smaller head, a simpler inclosing tube of nickel silver, sealing against moisture instead of using drying material, and lead connections with fewer, larger, more thoroughly insulated and connected strands, have also been introduced. Elec. heaters similar in construction to the resistance thermometers have high capacity, very low lag, usually under 3 sec., and are easy to construct. For details of construction the paper should be consulted.

W. P. WHITE

Laboratory thermometers. W. D. COLLINS. *J. Ind. Eng. Chem.* 13, 240-1 (1921).—Specifications. A thermometer ranging from -20° to 150° is more useful than -10° to 100°, and the shorter scale divisions are actually better for estn. of tenths, for most people.

W. P. WHITE

Apparatus for ultrafiltration according to Gans. LEONOR SARLO VILLEGAS. *Contr. estad. ciencias [La Plata], Ser. mat. fis.* 2, 415-8(1919).—A simple, transportable app. for ultrafiltration is described, which is particularly suitable for colloidal solns. of metals. Solns. of Ag, hemoglobin, albumin, and milk, among others have been investigated, and crystalloids which, for example, have been mixed with As, have been sepd. quant. The app. consists of a glass cylinder (9 cm. high and 7 cm. in diam.) provided with bronze disks as bases, which hermetically seal the cylinder by interspersed rubber rings. The upper disk has two openings, one for the manometer and the other for the pressure pump. At the bottom, between rubber ring and bronze disk, a thin,

metallic plate is clamped which serves as support for the ultrafilter. Pt is a suitable material for the plate, but Ni or Al can be used; it is provided with a number of holes, 1 mm. in diam., to permit the passage of the filtrate. The following method is used in prepg. the filter. Guncotton (12.5 g.) is thoroughly moistened with alc., and as much ether is added as is required to bring the vol. of the mixt. to 500 cc. A portion of this soln. is brought onto a glass plate and dipped in water; when the mixt. has set a gentle movement of the plate causes the thin film to become detached. Filters of this type are permeable to colloids. In general, permeability depends greatly on the acidity, and is markedly increased by the presence of small amts. of AcOH (about 0.5%). Colloid filters have also been investigated; variations of the soln. have been examd., and very satisfactory results are recorded with mixts. of equal parts of alc. and ether. The permeability of the colloid filters for colloids depends not solely on the amt. of AcOH added, but also on the time which has elapsed since the addition was made. A colloid filter to which as much as 6% of AcOH has been added gives a completely permeable filter if it is used immediately after being prepd.

J. C. S.

The automatic separator in esterification and other preparations. I. N. HULRMAN, ANNE W. DAVIS AND H. T. CLARKE. *J. Am. Chem. Soc.* 43, 366-70 (1921).—An app. of very simple construction for the continuous sepn. of 2 liquids of limited mutual soly. and differing in d. by not less than 2% is described; it consists essentially of a U-tube with a side arm on each limb, that on one limb being slightly higher than the side arm on the other limb; when the app. is working the lighter liquid flows continuously out of the higher, the heavier liquid out of the lower side arm. A number of instances are given in which the app. has been used in connection with distns. of a mixed liquid where it is desired to return one of the liquids to the distg. flask; viz., steam distn. of PhNH<sub>2</sub> and similar liquids, sepn. of BuOH or iso-AmOH from H<sub>2</sub>O, prepn. of Bu<sub>2</sub>O, dehydrating oxalic acid by boiling with CCl<sub>4</sub>, prepn. of (CO<sub>2</sub>Et)<sub>2</sub> from the crystd. acid and alc. in CCl<sub>4</sub>, prepn. of Et tartrate in the same way, prepn. of (CO<sub>2</sub>Bu)<sub>2</sub> from the crystd. acid and the alc. and prepn. of trimethylenechlorohydrin from the glycol and concd. HCl.

CHAS. A. ROULLER

Tests of miners' flame safety lamps in gaseous, coal-dust-laden atmospheres. L. C. ISLEY AND A. B. HOOKER. *Bur. Mines, Repts. of Investigations* 1920, No. 2199.—Coal dust powdered to 200-mesh was added to the methane-laden atm. of the special gallery at the Pittsburgh Sta. and its effect on various types of safety lamps noted. Thirteen failures from a total of 50 tests with unbonnated lamps occurred, 2 of which were caused by the presence of coal dust. The authors conclude that unbonnated lamps are less safe in atms. containing the dust, and future tests of flame lamps are to include a certain proportion made in dusty atms.

H. L. OLIN

"Ideal" cutoff valve. C. MARSCHEIDER. *Chem. App.* 8, 16-8 (1921), 5 cuts. —Description of the Borsig "Ideal" valve.

J. H. MOORE

Small compressor for chemical work. ANON. *Z. angew. Chem.* 34, Aufsatzteil, 15 (1921).—The compressor is driven by an eccentric shaft and sliding block arrangement which dispenses with piston rods. The resultant short stroke and high speed permit compact design and light wt. Four sizes are available, with capacities of from 3 to 30 cu. m. of free air per hr. delivered at 6 atm. pressure. The unit may be used for compressing gases or as a vacuum pump.

I. T. THORNTON

Centrifuge, Bauart "ter Meer," for separating solids from liquids. M. KELLNER. *Z. angew. Chem.* 34, Aufsatzteil, 9-15 (1921).—The centrifuge described is of the self-discharging type for continuous operation, and is designed for large-scale work, such as dehydrating sewage. It is an improved modification of the "Schafer ter Meer" centrifuge, which is also self-discharging but which depends on a screen for the sepn., with intermittent bottom discharge. The "ter Meer" centrifuge is under-driven, operates

at 1000 r. p. m., and requires about 12 h. p. for the main drive and 5 h. p. for the auxiliary drive which operates the valve-closing gear and discharging device. The machine as installed at Hanover handled a feed of 11 cu. m. per hr. of sludge containing 93% H<sub>2</sub>O. The cake formed from this amt. of feed had a vol. of 2.2 cu. m., a wt. of 2200 kg. and an av. water content of 65%. The size of the machine is not given. The principal feature of the "ter Meer" machine is the sliding cylindrical outer shell, which itself forms the separator basket when raised in operating position. As the basket fills with sludge, the clear liquid overflows the top and is discharged through an outlet pipe at the top of the outer casing. When the basket is filled with solids the inlet valve is closed, the shell drawn down away from the basket spider and the cake is discharged into a lower outlet hopper. An auxiliary device provides for return to the inlet line of thin sludge, left in the center of the basket when it is about to be discharged. The movement of the shell is automatically controlled by an oil pressure system, adjusted for a predetermined time cycle but variable at will. A chart of volume reduction of the sludge in terms of % dehydration is given.

I. T. THORNTON

The colloidal mill and its use—(Block) 13.

Dissolving, crystallizing and calcining apparatus. A. ROY. U. S. 1,369,840, Mar.

1. Dissolving, crystg. and calcining app. are connected together for the convenient prepn. of cryst. MgSO<sub>4</sub> and MgO or other materials. Excess heat from the calcining app. is successively supplied to the crystg. and dissolving app.

Hardness-testing apparatus. P. V. VERNON. U. S. 1,369,993, Mar. 1.

Calcining furnaces. A. V. GOWEN-LOCKESNE. Brit. 148,497, July 10, 1920. The pat. relates to the manuf. of refractory or abrasive products from siliceous rocks, refractory clays, MgO, dolomite, chrome iron, spinel, agglomerated powders of emery and corundum, and Zr and Ce earths, and comprizes forms of furnace adapted for the complete calcination of the raw materials. A suitable construction is specified.

Mixing; treating solids with liquids. K. PEISTERER. Brit. 152,649, Oct. 18, 1920. An app. for producing an intimate mixt. of a solid and fluid, or for producing solns., e. g., satd. clear lime-water for the purification of feed water for boilers, consists of a jet-pump placed in a vertical mixing tube and operated by the solvent, the liquid from the pump passing through the substance to be dissolved into the mixing tube, any solid settling in the mixing tube being drawn into the pump and again circulated.

Furnaces; cooling. A. BIGOR. Brit. 152,602, Oct. 8, 1920. An app. for calcining, baking, etc., applicable also for cooling materials, comprizes a heat-insulated chamber having hollow walls loosely packed with masses of heat-absorbing material, such as bricks, through which, as also through the chamber itself, hot (or cold) gases are caused to flow. The invention is applicable for drying clays, etc., dehydrating gypsum, etc., treating NaHCO<sub>3</sub> and silico-limestones, and baking bread.

Stuffing-boxes for vacuum vessels. GLEINRICHTER-AKT.-GES. Brit. 153,585, Nov. 8, 1920. A liquid-seal joint for a vacuum vessel such as a metallic vapor rectifier has a solid jointing-device consisting of asbestos, leather, rubber or metal constructed in the form of a stuffing-box, the sealing liquid being water glass, oil, or tar products. Recesses are provided inside the joint to catch any sealing liquid passing the joint.

Heating by electricity. S. H. CALVERT. Brit. 155,637, Sept. 20, 1919. A flow heater for H<sub>2</sub>O comprizes a flattened tube of Cu or other highly conductive material clamped between heating elements and asbestos strips by plates and bolts. The heating element consists of wires or strips wound round thin strips of mica or other insulating material and enclosed between wider strips which overlap the core. A suitable construction is specified.

Electron-discharge devices. J. E. LILIENFELD. Brit. 155,554, Mar. 9, 1920.



The electron stream of a high-vacuum tube for use as a detector, relay, oscillation-generator, or Röntgen-ray tube, is produced by a discharge across a small gap between 2 electrodes. One or both electrodes are preferably formed with a pointed end or sharp edge, and the gap is of the order of 3 mm. Adjustment of the length of the gap may be effected by means of 1 or 2 heating-coils mounted inside the hollow Cu or Fe supports for the electrodes, or by means of a press acting on an elastic glass or metal part. The electrodes of W, Ta or Pt, may be arranged symmetrically or otherwise, and may be of disk, annular, hemispherical, or paraboloidal shape, or may be arranged as co-axial cylinders or cones, or one electrode as a cone and the other as a disk. An incandescent filament may be used for expelling gases from the electrodes during exhaustion. A suitable construction is specified.

Röntgen-ray and vacuum tubes. ELEKTRISCHE GLÜHLAMPENFABRIK WATT AKR.-GAS. Brit. 152,617, Oct. 16, 1920. A ring or cup for making connection between an electrode and glass is formed of a metal or alloy, such as an alloy of Fe and Ni, the coeff. of expansion of which differs only slightly from that of glass, the metal, etc., being coated with Pt, Cu, or other metal which makes a good fused joint with glass. The edge of the ring or cup may be bent over, the coating being applied to one side only and around the edge.

## 2—GENERAL AND PHYSICAL CHEMISTRY

W. E. HENDERSON

Some relations between the solubilities of solutes and their molecular volume. SHINKICHI HORIBA. *Trans. Faraday Soc.* 15, Pt. 3, 178-85(1920).—H.'s previous work on the relation between soly. and mol. vol. is reviewed. It was shown that they are in almost linear relation and that this holds for different temps., 0°, 20°, 30°. He next develops the equation:  $\ln \sigma = -(N_p/RT)(\alpha - \beta) - \ln \sigma - (N/RT)a$ , where  $\sigma$  = concn. of the solute in the satd. soln.,  $N$  is the Avogadro const. and  $\nu = (4/1.1)(\sqrt{V/v} + 1)^2$  = the number of mols.  $\nu\alpha$  = amt. of work done in sepg. mols. of the solvent from each other.  $\nu\beta$  = work done by the attraction of the mols. between solvent and solute. This equation is shown to hold for a number of alkyl halides using data by Rex. That is, all chlorides, bromides and iodides lie on straight lines. It is also shown to apply to some hydrocarbons of the benzene series. E. H. DARBY

A graphic presentation of the equation of state. A. MOLLIER. *Physik. Z.* 21, 457-63(1920).—Starting with the van der Waals equation in the form:  $pv^2/T = [Rv^2/(v - b)] - (a/T)$  and setting  $pv^2/T = \gamma$ ,  $\zeta$  = density and  $l = 1/b$ , M. obtains the equation:  $\gamma = \{Rl/\zeta(l - \zeta)\} - (a/T)$ . He then plots  $\gamma$  against  $1/T$ , obtaining a symmetrical parabolic curve. He plots a series of such curves for CO<sub>2</sub> for several temps. between 40° and 198° using Amagat's data. Two other figures are given, showing the  $s/r^2$ ,  $Rd$  and  $s/R^2$ ,  $1/t$  diagrams, using the empirical equation:  $s/V^2 = [P/(Rd)^2] - (1/Rd) = B + C(Rd) + D(Rd)^2 + E(Rd)^3 + F(Rd)^4$  which is related to the reduced van der Waals equation.  $s/R = (pv^2/Rt) - v = [1/(3-d)] - (9/8t)$ . The treatment is mathematical throughout. A table is given of the consts. of the gases, H, He, N, air, O, CO<sub>2</sub>, ethylene, isopentane and ether. E. H. DARBY

Nernst's heat theorem and chemical constant. EICHI YAMAZAKI. *J. Tokyo Chem. Soc.* 41, 19-35(1920).—This is a theoretical paper, the argument depending on mathematical deductions. In the well known formula  $\ln K_p = - \int \frac{dT}{RT^2} \left\{ Q_p + \int \sum C_p dT \right\} + \text{const.}$ ,  $K_p$ , a const. for the gaseous chem. equil., is a function of

temp. Before Nernst's heat theorem was put forth, the last const. of the integration of this formula had been detd. for each substance. Although Nernst gave this as a known const. for a temp., his explanation is not perfect, giving no theoretical meaning for this const. Sackur's explanation is also far from perfect, his calcd. values being too far from exptl. data. By using Gibb's theory of chem. energy, Y. derived a simple formula which not only gives the real meaning for this const. of integration, but also his calcd. values show perfect agreement with Nernst's values (comparisons are given for 21 compds.). S. T.

The determination of the hydrogen number by indicators. L. MICHAELIS AND A. GYEMANT. *Biochem. Z.* 109, 185-210(1920).—An extensive description is given of the detn. of the dissociation curves of the indicators:  $\beta$ -Dinitrophenol,  $\alpha$ -dinitrophenol, phenolphthalein, *p*-nitrophenol, *m*-nitrophenol and *m*-nitrobenzenecarbazolic acid in various buffer solns., thus giving the range of availability of these substances. The theory of the salt error of the indicators is discussed and it is stated that salts with bivalent cations and salts with bivalent anions cause greater deviations than do univalent cation and anion compds.; that the salt error produced by bivalent cations is but little more than that produced by the bivalent anions; and that the error caused by the bivalent cations is not entirely independent of the  $p_H$ . In the presence of the usual inorg. salts the salt error would indeed be overwhelming, if it were not for the "Bjerrum effect," or as Arrhenius has expressed it, that the dissociation const. of the indicator acids is increased by salts. The temp. coeff. of the indicator const. also is discussed and practical applications of the findings are described, all of which can be summarized in the statement that when a one-color indicator is added to the soln. to be studied, there usually is obtained a depth of color lying between the max. color seen when the reaction is strongly alk. and the quite colorless condition at the extreme acid end. Now when this color is compared with the max. color obtained with the same indicator by strong alkali there is obtained the "color degree" or the dissociation degree ( $\alpha$ ) of the indicator acid in the soln. studied, and from this  $\alpha$  can be detd. by the formula  $h = k(1 - \alpha)/\alpha$  or by logarithms  $p_H = p_k + \log [x/(1 - \alpha)]$ ,  $p_k$  denoting the negative log. of the dissociation const. of the indicator. The second member is a function ( $\varphi$ ) of the colorimetrically detd. value  $\alpha$ . F. S. HAMMETT

Friedrich Dolezalek. ALFRED SCHULZE. Charlottenburg. *Z. Elektrochem.* 27, 89-92(1921).—A brief survey of the work of the late Friedrich Dolezalek. H. J. C.  
Ignaz Stroof. B. LÆPSIUS. *Z. Elektrochem.* 27, 92-4(1921); *Ber.* 54A, 101-7 (1921). A brief survey of the work of the late Ignaz Stroof. H. J. C.

New York Chemists' Club confers honorary membership. ANON. *J. Ind. Eng. Chem.* 13, 355-7(1921).—Brief biographical outlines are given of the men on whom honorary membership was conferred, namely, Ernest Solvay, Henri L. LeChatelier, Sir Edward Thorpe, Giacomo Ciamician, John Uri Lloyd, W. H. Nichols, Edgar F. Smith and Edward Wesson. In addition brief reports are made of addresses by Jacques Loeb and Irving Langmuir on "The chem. and physical behavior of protein solns." and "Influence of physics on modern chem. thought," resp. E. J. C.

Has the existence of atoms and molecules been proved? A. VON ANTROPFF. Karlsruhe. *Z. angew. Chem.* 33, I, 321-4(1920).—In order to avoid a discussion of the question of the existence of material objects apart from the sensations which they produce, A. restates the above question as follows: Is the existence of atoms and mols. just as real as that of the visible and tangible objects of the external world? He states as an axiom: If a substance is composed of similar parts, these parts have the same degree of reality as the substance. He then proceeds to show that many experimental facts, generally considered to prove the molecular structure of matter, actually prove no such thing. An exact proof of the existence of atoms and mols. is found in the phen-

omena associated with canal rays. This paper should be of considerable interest to teachers of elementary chemistry and to other chemists who sometimes have occasion to answer the question stated in the title.

D. MACRAE

Vibrational frequencies of the halogen acid molecules. W. F. COLBY. *Phys. Rev.* 15, 140-1(1920).—Abstract. Imes (C. A. 14, 3366) shows that the absorption bands of three halogen acids can be closely represented by the formula  $\nu = \nu_0 - \frac{1}{n^2}$  — $\frac{1}{n^2}$  where  $n$  indicates successive integers. In accordance with the Bjerrum postulate which ascribes these absorptions to a combination of rotation and interatomic vibration of the mol., the present paper undertakes an investigation of a familiar molecular model in the hope of testing the above formula. An expression for vibrational frequency is obtained that agrees closely with the Imes formula.

D. MACRAE

Supplement to my work "a direct measurement of thermal molecular velocities." OTTO STERN. *Z. Physik* 3, 417-21(1920).—S. shows that the atoms leaving his Ag surface do not have the velocity  $\sqrt{3RT/M}$  corresponding to thermal equil. with the liquid Ag, as calcd. before (cf. C. A. 14, 2881), but are faster moving mols. with an av. velocity  $\sqrt{4RT/M}$ . This gives  $v = 672$  m./sec., and S. makes new measurements at a higher speed of rotation, giving exptl. values of 675 and 647.

F. C. HOYT

Certain numerical relations which the atomic weights present. EDMOND JANDRIER. *Mon. sci.* 10, 169-72, 193-8(1920).—The at. wts. of the alkali metals, and the differences between their successive at. wts. may be represented by the formula,  $m7 + n16$ . The at. wts. of Tl, Ag, and Au, also follow this rule if they are included in the alkali group

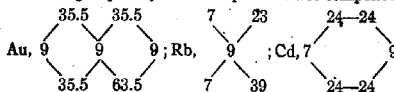
$$\begin{array}{cc} 108 & 204 \\ \swarrow & \searrow \\ \text{as side members, thus, } 7-23-39-85-133 & \text{The at. wts. of the MO group have} \\ & \searrow \\ & 197 \end{array}$$

the general formula,  $19 + m15 + n16$ . In these formulas the number 16 represents a grouping of atoms, probably formed of two groups, 7 and 9, which, by its combination with the group 7 of Li, before the formation of the latter, has been able to form Na, and by its combination with the group 24 of Mg, to form Ca. The at. wts. of Bi, Cd, and Hg are related to this group in the same way as are the at. wts. of Tl, Ag, and Au to the alk. metal group. The parallelism between the numerical compn. of the at. wts. of groups I and II is shown by a comparison of some of the corresponding members: Li = 7, and Gl = 9; Na = 7 + 16, and Mg = 9 + 15; K = 16 + 7 + 16, and Ca = 16 + 9 + 15, Ce =  $(4 \times 16) + \text{Li} + \text{Na} + \text{K}$ , and Ba =  $(4 \times 16) + \text{Gl} + \text{Mg} + \text{Ca}$ . This parallelism is made more evident by schematic structural formulas of the at. wts. Thus, for Rb, 16-7-16-7, and for the corresponding Sr, 15-9-15-9. Similar

$$\begin{array}{cc} 16-7-16 & 16-9-15 \end{array}$$

formulas are given for all members of the groups. It is noted that the lighter elements are represented by open asymmetrical chains, whereas the more dense elements may be represented by closed symmetrical schemes. For the group  $\text{M}_2\text{O}_3$ , with the exception of Ga, the at. wts. are represented by the formula  $11 + m16 + n17$ . Similar relations in groups 5 and 6 are presented. The at. wts., and their differences, of the group of elements, F, 19; Cl, 35.5; Cu, 83.5; Br, 80; Ag, 108; I, 127; (61), 152.5; Au, 197, have the general formulas,  $19 + m16.5 + n28$ , and  $19 + m35.5 + n9$ . (61) is a hypothetical element of at. no. 61, and at. wt. 152.5. The at. wts. of these elements, except the first two, may also be considered as formed by the addition of 9 to numbers representing the at. wts. of members of the group, i. e., at. wt. =  $e \pm \sigma P + 9$ . This formula applies also to the at. wts. of the monatomic members of group I, as do also the

relations  $17 + m23 + n9$ , and  $17 + m9$ . For group II, the at. wt. =  $\Sigma P + 7 = 19 + m24 + n7$ . Schematic structural formulas are given showing how the at. wts. of elements of these several groups may be built up from these component numbers, e. g.,



Several different schematic groupings are possible for the same element. The validity of the use of whole numbers to represent the at. wts. is discussed, and such whole numbers are called "numbers of constitution." Numerical relations between the series of odd and of even at. wts. are given.

R. H. LOMBARD

A comparison of the atomic weights of terrestrial and meteoric nickel. I. The reduction of nickelous oxide. GREGORY P. BAXTER AND LEON W. PARSONS. *J. Am. Chem. Soc.* 43, 507-18(1921).—The nickelous oxide prepd. by igniting the nitrate at about 1000° contained 0.11% of occluded gases. After correcting for this the at. wt. of terrestrial Ni was found to be 58.70 and that of meteoric Ni 58.68, a difference within the limit of the expld. error.

JEROME ALEXANDER

Surface layers upon metals. HANS HAUSCHILD. *Ann. Physik* 63, 816-44(1920).—A complete study is made of reflection and polarization from metallic mirrors by means of an app. in which the mirror was adjusted perpendicular to the axis of a spectrometer and enclosed in such a way that vacuum or an atm. of a gas could be maintained in studying the effect upon the metal under consideration. A combination of Senarmont compensator and Savart plate next to an analyzing nicol was used. The original paper should be consulted for the mathematical derivations shown by means of curves.

G. L. CLARK

Molecular energy in gases. J. A. EWING. *Proc. Roy. Soc. Edinburgh* 40, 102-11 (1921).—See C. A. 14, 2435.

E. J. C.

Deduction of molecular structure from the liquid crystal condition. D. VORLÄNDER. *Physik. Z.* 21, 590-1(1920).—The valence directions of O and S in bivalent compds. form angles of about the same value as the valence angles in quadrivalent carbon. The displacement from the symmetrical arrangement is attributed to secondary valence forces. The article is short and is followed by a much longer discussion in which there are many participants.

C. R. PARK

The molecular forces of fluid crystals and their relation to known forces. O. LEHMANN. *Z. Physik* 2, 127-45(1920); cf. C. A. 14, 2280, 2886.—The theory of "atomic grouping" as developed by Bragg and Bragg from their observations with the X-ray spectrometer, has been applied by P. v. Groth to chem. crystallography (*Die Naturwissenschaften* 7, 651(1919)), liquid crystals being explained on the incorrect assumption that their mols. are oriented by surface tension and must, therefore, be radial in spherical drops. However, as the drop is not freely suspended in air but is surrounded by a fluid, its structure is more complicated, the mol. axes pointing, relatively, to the spherical surface, differently in different places. With plane surfaces there is a similar orientation unless there is contact with air or with a solid adsorption film. If such an adjacent surface is amorphous, "clinging" occurs, the molecular platelets arranging themselves parallel to the surface, thus making the optical axis perpendicular to it. The structure of liquid crystals is more complicated than that of solid crystals, being usually flaky. The normal form of the hydrate of ammonium oleate is a double sphere, an ellipsoid of revolution or a cylinder. But the surface tension is obviously not greater

at those parts of the crystal surface having the greater curvature, as might be expected, which points to an anisotropic distribution of molecular forces (directional forces). Amorphous substances are to be viewed as mixts. of various mols. whose directional forces (at the existing temp. balance) are unable to establish a regular lattice; nevertheless, they develop an elasticity approaching that of the crystalline modification of the same substance. True fluids which have no real elasticity, exhibit no molecular directional forces such as are shown with such intensity by fluid para-azoxyphenetole, whose mols. strive to become parallel to those adsorbed by the glass slide. Crystals of ammonium nitrate, when subjected to plastic deformation, do not resume their original shape, despite thermal agitation and molecular directional forces. The molecules composing liquid crystals act like astatic magnetic systems or systems of rotating electrons. If they are far apart the magnetic attraction appears as cohesion; but if very close directional forces take precedence and lead to a lattice structure and to *anisotropic surface tension*. Such molecules are anisotropic themselves, being either rod- or disc-shaped. The coalescence of liquid crystals proves that their internal friction is also anisotropic, for a small rod when added end on to another causes no increase in diameter, but produces a bulge if added sideways. The author considers and illustrates many other complicated types of structure in liquid crystals, including conic and biconic forms; also the swelling of liquid crystals and *myelin forms*. "Liquid crystals in common with solid crystals are able to *grow* (preserving meanwhile their anisotropy); they are *phases* in the thermodynamic sense, whereas amorphous and colloidal substances are not, even if these latter show an accidental double refraction. Their molecules strive to become as *nearly* parallel as possible; but this does not occur even with solid crystals if they are continuously bent or twisted."

JEROME ALEXANDER

**The nature of secondary valence.** HOMER W. SMITH. *J. Phys. Chem.* 25, 160-9 (1921).—A preliminary communication. Physicists in dealing with cohesion usually assume that the attraction of mols. is due to "stray electric fields" surrounding the electrons of the atom; also that mol. configuration plays an important part in detg. the attraction between two mols., and that the force acting may be treated on the basis of the inverse square, or the inverse fourth, however, or some such mathematical function of the distance supposedly sepg. the mols. "It is within the province of this paper to show that all three of these assumptions are erroneous. Evidence derived from a study of org. compds. will be presented to show that the forces acting between mols. are comparable to those forces in the atom which are responsible for atomic structure, in that they are rhythmic in nature and are consequently not subject to treatment under familiar electro-magnetic laws." When mols. are in equil. with regard to their interacting elec. forces the factors brought into play are (1) their respective intensities of attraction and (2) their respective mol. vols. The latter factor has been neglected. "We have in some measure been misled by the graphical formulas which we draw upon the black-board into believing that mols. always have rigid and characteristic configurations." In molecular physics "there is never any indication that any mol. has any other shape than that of a perfect sphere. . . . every mol. behaves as though it completely fills a definite space which has three-dimensional symmetry." At the interfaces of liquids, owing to restriction of mol. motion, the mol. behaves as though its secondary valence were localized at one or more points, although in general it acts as though distributed uniformly over the surface of the mol. "domain" or localized at its center. Details regarding partition coeffs. (distribution of a solute between two immiscible liquids—to be given in next paper) show that in any series of compds. having the same intensity of secondary valence, the partition coeff. is a simple logarithmic function of the mol. vol.; also that secondary valence is rhythmic, *i. e.*, it varies in different mol. species by definite and related amts. These variations are attributable to changes in the state

of one or two particular atoms in the mol. and have their origin in the mode of chem. combination. Secondary valence associated with a given mol. species depends also on the nature of its environment, involving some readjustment of the valence electrons (possible mechanistic cause for dissociation). The rhythmic atomic mechanism of secondary valence is presumably analogous to the stable electronic orbits postulated to explain Planck's energy radiation quantum. So far as the author is aware, "this is the first experimental demonstration of a quantum, or rhythmic variation in fundamental forces." The results bear on both the nature of solution and the structure of the atoms.

JEROME ALEXANDER

The critical quantities of mercury in connection with the increase of the molecular attraction on dissociation of the double molecules. I. J. J. VAN LAAR. *Proc. Acad. Sci. Amsterdam* 23, 267-81(1921).—A survey of all expl. work on the detn. of the crit. values for Hg leads to the following as the most probable values:  $t_c = 1700^\circ$  Abs. ( $1427^\circ$ ),  $p_c = 1100$  atm.,  $v_c = 215.7 \times 10^{-3}$ , and  $d_c = 4.15$ . These require the assigning of lower values to the van der Waals consts.  $a$  and  $b$ , viz.,  $10^6 b_c = 120$  and  $10^6 a_c = 100$ , than those formerly calcd. by the author. These crit. quantities take into account the complications arising in the possible dissoc. at  $t_c$  of the double mols. to a slight extent, or  $\text{Hg}_2 = 2\text{Hg}$ . It is not because the value of  $a_c$  itself, in consequence of a slight degree of dissoc. ( $x$ ), is appreciably increased, and, therefore,  $T_c$  and  $p_c$  which are both proportional to  $a_c$ , are likewise increased in the same degree—for this increase of  $a_c$  for so small a value of  $x$  is much too small—but because, in consequence of this dissoc. in connection with the very high value of  $da/dx$ , the formula which expresses  $T_c$  in terms of  $a_c$  obtains a factor which is a function of  $x$  and  $da/dx$ , and through which  $T_c$  is increased by 30% and  $p_c = [RT_c/(v_c - b_c)] - (a_c/b_c)$  by 300% or more. These relations are derived mathematically in a paper immediately following. For the calcn. of  $D_1 + D_2$ , referring, resp., to liquid and vapor, the following expression agrees accurately with expl. values above  $400^\circ$ :  $D_1 + D_2 = 13.5956 - 0.0024507t + 0.062089t^2 + 16.4 \times 10^{-4} (t/100)[8.35 - t/100]^{3/2}$ . At  $1427^\circ$  this value is 8.30 and thus  $D_c = 8.30/2 = 4.15$ . A check is obtained by extrapolation of the empirical relation  $D_1 - D_2 = C\sqrt{1 - (T/T_c)}$ . The values of  $\gamma$ , the reduced coeff. of direction of the straight line diameter of mean densities, are 0.72 between 1000 and  $1427^\circ$ , 0.49 between 0 and  $300^\circ$ , and 0.51 between 0 and  $1000^\circ$ , while 0.50 is that due to ideal substances with  $a$  and  $b$  invariable. Thus below  $1000^\circ$ , Hg behaves as an ideal substance, while above this temp. there is an appreciable curvature towards the side of large vols. Independent calcons. of  $r = v_c/b_c = 1.8$ , and  $\theta$  and  $\pi$  the factors of  $T_c$  and  $p_c$ , resp., consequent to a small degree of dissoc., confirm the above crit. quantities. G. L. CLARK

The critical quantities in the case of association, when the molecular attraction is considerably increased on dissociation of the molecules to the isolated atoms, also in connection with the critical quantities of mercury. II. J. J. VAN LAAR. *Proc. Acad. Sci. Amsterdam* 23, 282-98(1920); cf. preceding abstr.—In the preceding paper the choice between different values of  $r = v_c/b_c$  remained open because of lack of a close definition. In this paper, which is purely theoretical and mathematical, is examd. what follows from  $dp/dv = 0$  and  $d^2p/dv^2 = 0$  in the case of great values of  $\Delta\sqrt{a}$  on dissoc. Then  $r$  and  $\theta$ , the factor of  $T_c$ , are derived as functions of  $x$  and  $\Delta\sqrt{a}$ , from which  $\pi$ , the factor of  $p_c$  follows. By setting up equations for the thermodynamic mol. potentials in a mixt. of double and single mols. of Hg,  $(dx/dv)_c$  is derived and found to be negative at the crit. point, i. e.,  $x$  decreases with increasing vol. because as  $x$  first increases this increases  $a$ , the term expressing greater attraction, but this causes the vol. to decrease until the decrease exceeds the original increase. The differential quo-

tient  $(dp/dv)_t$  is next derived by including the value of  $(dx/dv)_t$ , and set equal to zero, from which  $RT_c$  is found in terms of  $v_c$  and  $b_c$ ; whence

$$1/RT_c v_c = \frac{\{(2-x)\alpha^2 - 2x(1-x)\alpha\Delta + (1-x^2)(1-b^1)\Delta^2\}}{(2-x)(1+x)(1-b^1) - x(1-x)}$$

where  $x = \text{deg. dissoci.}$ ,  $\alpha = \frac{v-b}{b} \sqrt{a}$ ,  $\Delta \sqrt{a}$ , and  $b^1 = \left(\frac{\partial b}{\partial v}\right)_x$ , which simplifies if

$\Delta = 0$  or if  $x = 1$  (all the mols. single). If  $b^1 = 0$  and  $r = v_c/b_c = 3$ , then  $RT_c = 8/27$ ,  $(a_c/b_c)$ . However, the values of  $r = v_c/b_c$  cannot be obtained until the second differential quotient  $(dp/dv^2)_t$  is set equal to zero at the crit. pt. The fundamental equation derived for its detn. is

$$3(1 + \tau\rho(\rho - 2)) + \frac{(1 - \tau\rho)^2}{1 - \tau} \beta = \frac{\rho}{\phi(1+x)} \left[ 2 - \tau\rho + \frac{\tau\rho - 1}{1 + \tau} \left\{ (1 - \tau\rho)^2 - \omega(\rho - 1)^2 \right\} \right]$$

where  $\rho = (1+x)(1-b') \frac{\Delta}{\alpha}$ ,  $\tau = \frac{x(1-x)}{(2-x)(1+x)(1-b')}$ ,  $\phi = \frac{\Delta\sqrt{a}}{\sqrt{a}}$ , (hence  $\rho = \phi$

$(1+x)(1-b') \frac{v_c}{v_c - b_c}$ , or for small  $x$ ,  $3(1-b') \frac{r}{r-1}$ ), thus being in connection

with  $r, \beta = \frac{-b''v}{1-b'}$ ,  $\omega = \frac{1}{1-b'} \left( 1 - \frac{2}{(2-x)^2} \right)$ . For Hg, if  $x$  is small  $\phi = \frac{3}{1+3x}$ ,  $\tau$  is

very small and  $\omega = \frac{1}{2(1-b')}$ . It follows that  $RT_c = \frac{2}{1+x} \frac{2(r-1)^2 a_c}{(1-b')^2 b_c} \times \frac{1-\tau\rho(\rho-2)}{1-\tau}$ ,

and  $\left(\frac{dx}{dv}\right)_t = \frac{1}{v_c - b_c} \frac{x(1-x)}{2-x} \frac{1-\rho}{1-\tau\rho}$ . It is then possible to evaluate the factor  $\Theta$

in  $RT_c = \frac{2}{1+x} \frac{8}{27} \frac{a_c}{b_c} \Theta$ , which is 1 if  $r = 1.5$ .

G. L. CLARK

The diagram of state of carbon. J. A. M. VAN LIEMPT. *Z. anorg. allgem. Chem.* 115, 218-24(1920).—Utilizing the new data of Kohn (*C. A.* 15, 782) and van Laar (*C. A.* 15, 1435) further criticism is made of the work of Lummer on the temps. of C arcs and the possible existence of molten C below 4700° (cf. *C. A.* 9, 143; 11, 2301; 12, 1015). The observations of Lummer pointed to the fact that at 7700° and 22 atm. C is solid, while at 4200° between 0.2 and 2 atm. it is liquid. By the use of van Laar's formula  $\log p = -47120/T + 8.5$ , and the Clapeyron equation from which the density of liquid C is calcd. to be only 0.0003, the absurdity of liquid C below 4700° is pointed out.

G. L. CLARK

The liquefaction of carbon. EUGEN RISHKEVICH. *Z. Elektrochem.* 27, 57-64 (1921).—The paper gives an account of some expts. which show that small portions of C electrodes employed in elec. furnaces undergo liquefaction. It is maintained that these expts. remove the last doubt that the m. p. of C can be attained. The expts. were carried out with a small elec. furnace heated by direct resistances of C. The heating chamber of the furnace was formed by 4 C plates 15 mm. thick and 25 cm. long. Two of these plates (7 cm. wide) formed the side walls, while the other 2 (10 cm. wide) formed the bottom and top of the C box. The new electrodes had an ash content of 8%. A current of 500-560 amp. was applied for 3-4 hrs. After being heated in the furnace for 2-4 hrs. the electrodes were converted into 99.6 to 99.9% C. In some instances the electrodes during heating underwent a change in form which was so remarkable that it can only be explained on the assumption that the C became liquid during the heating. This change in form only occurred with electrodes that had been converted

into pure C. The solidified melt consisted of pure C and was soft, being easily cut with a knife. The cut surface appeared smooth and possessed a metallic luster. Not a trace of granular or scaly structure could be observed, even under a magnification of 100-200 diams. Numerous photomicrographs are given, some of which show most distinctly solidified drops of C. In conclusion it is pointed out that at ordinary pressure, it is very probable the temp. interval in which C melts is very small. H. J. CRRIGHTON

The critical temperature of mercury. G. MEYER. *Physik. Z.* 22, 76-8(1921).

—From surface tension data for Hg between 20 and 367° the value 1474° has been obtained for the critical temp. of Hg, by means of the Eötvös equation. This value is considerably higher than values obtained by other investigators. It is shown that while above 270° Hg consists wholly of monatomic mols., below this temp. association sets in, the association factor gradually increasing to 1.133 at 20°. The equil. const. of the dissociation of the double into simple mols. and the heat of dissociation have been calcd. at 20° intervals between 20° and 280°. The equil. const. and the heat of dissociation vary, respectively, from 0.338 and 1431 cal. at 20° to 10515 and 15190 cal. at 280°.

H. JERMAIN CRRIGHTON

The dependence of the heat of evaporation of water on the temperature. F. HENNING. *Z. Physik* 2, 197-9(1920); cf. *C. A.* 13, 2802.—Formulas are developed for detn. of the temp. coeff. of water and a table is given of these with the corresponding heats of evapn. at temps. from 0° to 180°.

JEROME ALEXANDER

Comment upon my investigation: "The dependence of the heat of vaporization of water on the temperature." H. v. STEINWEHR. *Z. Physik* 2, 200(1920); cf. *C. A.* 15, 1245.—The formula is only proved from 30° to 180°. An extrapolation to the crit. temp. is clearly inadmissible. An extrapolation over 30° down to 0° not only seems legitimate but probably gives better results than any other method of detn. at 0°.

W. P. WHITE

Solubility of potassium bromide in bromine water. ALFRED F. JOSEPH. *J. Chem. Soc.* 117, 377-81(1920).—The soly. of KBr in water at  $32.4 \pm 0.02^\circ$  is 725.6 g. per 1000 g. H<sub>2</sub>O (av. of 4 detns.). The increased soly. of KBr in the presence of Br equals one-third of the Br concn. (between 0 and 382.1 g. of Br per 1000 g. H<sub>2</sub>O). With 382.1 g. Br, 1000 g. H<sub>2</sub>O dissolves 845.9 g. KBr. "KBr appeared to be quite insol. in pure Br, and it must, therefore, be concluded that the water is entirely responsible for keeping these large quantities in soln.; the limit of the solvent capacity of the water, even when it constitutes only 5% of the soln., has not been reached. There is, however, a maximum volume concentration of Br, the corresponding Br concentration being between 200 and 2000 g. per l.

JEROME ALEXANDER

Density of hydrochloric acid. J. FITCH KING. *J. Phys. Chem.* 25, 115-21(1921).—After pointing out the lack of agreement in data on HCl found in the literature and tabulating some of the figures calcd. to show the d. of 2 N HCl at 15° referred to H<sub>2</sub>O at 4°, K. details his careful detns. with the Davis pycnometer, giving a density of 1.0344 (literature variations from 1.0328 to 1.0357); concn. coeff. ( $\Delta D/\Delta C$ ) = 0.004986; temp. coeff. ( $\Delta D/\Delta T$ ) = 0.00025 between 15° and 20°.

JEROME ALEXANDER

Solubility of naphthalene in aqueous solutions of alcohols and fatty acids. JOHANNES CHRISTIANSEN AND S. ARRHENIUS. *Medd. K. Vetenskapsakad. Nobelinst.* 4, No. 2, 25 pp.—Soly. of naphthalene is detd. in solvents consisting of mixts. of H<sub>2</sub>O with varying amts. of CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, C<sub>3</sub>H<sub>7</sub>OH, HCOOH, CH<sub>3</sub>COOH, C<sub>2</sub>H<sub>5</sub>COOH, and C<sub>3</sub>H<sub>7</sub>COOH. When these results were compared with ballograms of these mixed solvents it was found that the substance in any series which had greatest power of solution was that of greatest balloelectricity. The mixt. which was balloelectrically neutral corresponded with the compn. of a probable hydrate and had a very small dissolving



power. Even this small power is probably due to slight dissociation. The relation  $c = AX^n$  represents the relation of the soly. of  $C_{10}H_8$ ,  $c$ , to the concn. of the solvent,  $X$ , in its aq. soln.  $A$  and  $n$  are consts., the latter being independent of temp. between  $0^\circ$  and  $25^\circ$ .

A. E. STEARN

Standardized method for the determination of solidification points, especially of naphthalene and paraffin. R. M. WILHELM AND J. L. FINKELSTEIN. *Bur. Standards, Sci. Papers* 340, 158-97 (1919).—The app. consists of a test-tube with thermometer and glass stirrer air-jacketed by insertion through the cork of a wide-mouthed bottle, which is immersed in a water bath. "The solidifying point corresponds to the first series of 5 or more readings, during which the temp. remains const. (change not over  $0.02^\circ$ ). Usually under-cooling will occur, in which case the const. temp. should be observed immediately after the undercooling ceases." For exact details and description of the special thermometer recommended and also general discussion, the original must be consulted.

JEROME ALEXANDER

The chemical potential of phenol in solutions containing salts, and the toxicity of these solutions towards anthrax and staphylococcus. J. S. LAIRD. *J. Phys. Chem.* 24, 664-72 (1920).—The ratio of partition of phenol between water or NaCl solns. and kerosene was detd. to be 4.6 for pure water, 4.2, 3.3, 2.2, 1.5 and 0.9, resp., for 2, 5, 10, 15, and 20% salt solns. and was fairly const. for dil. solns. The concn. of phenol in chemically equiv. solns. calcd. from these values agreed with the results of Miller (*C. A.* 15, 120). The toxicity of chemically equiv. solns. of phenol towards staphylococcus were found to agree fairly well except with very dil. solns. Distd. water was found to be toxic to the same cocci, probably on account of plasmolysis, and the resistance of various cultures varied widely, thus explaining the results of Loomis. The chem. equivalences of phenol solns. containing NaOBz, AcOH, KI,  $NH_4Cl$ ,  $NaNO_3$ ,  $NaC_2H_3O_2$ , KBr, LiCl,  $NaClO_3$ , or KCl were also detd. The toxicities of 4% phenol solns. containing these salts as detd. by Paul and Kronig (*Z. physik. Chem.* 21, 414 (1896)), agreed fairly well with their chem. equivalences except in the cases of AcOH, KI, and  $NH_4Cl$ .

J. S. LAIRD

The mechanics of solidity. V. T. SAUNDERS. *Nature* 106, 534-5 (1920).—In spite of the fact that if some substances are arranged in order of increasing coeff. of expansion (linear), they are very nearly in a series of decreasing hardness, thus pointing to a close connection between the mechanical properties and the fundamental physical constants, it is shown that hardness is entirely omitted in all formulas, such as those of Sutherland, Einstein and Debye on atomic frequencies, which tend to express the relationship of physical properties. This omission is justified because the moduli of elasticity, the ultimate strength, and the coeffs. of expansion of a substance are expressions of body or bulk properties and depend upon the state of equil. of mols. throughout the body; while on the other hand hardness of the resistance of a surface to deformation by mechanical means is entirely a surface effect analogous to the surface tension of a liquid.

G. L. CLARK

Temperature and degree of polymerization. W. HERZ. *Z. anorg. allgem. Chem.* 115, 237-40 (1920).—A test is made of the simple relation  $M_k/d_k : M_s/d_s = \text{const.}$  where  $M_k$  and  $M_s$  are mol. wts., resp., at crit. and b. ps. and  $d_k$  and  $d_s$  the corresponding densities, for liquids known not to associate and those which do. The const. is found to be 2.69 by using liquids such as chlorobenzene whose mol. wts. are the same at both temps. The ratio  $M_k/M_s (= 2.69 d_k/d_s)$  is found to be unity even for alcs.,  $H_2O$  and acetic acid. The same is true for temps.  $^{1/12}$  and  $^{1/2}$  of the crit. temp. instead of the boiling temp. ( $^{2/3}$  the crit. temp.). No explanation is given of the fact that the influence of temp. upon the mol. wt. and degree of polymerization cannot be observed even for the liquids which are certainly associated.

G. L. CLARK

The elasticity constants of sylvite. K. FÖRSTERLING. *Z. Physik* 2, 172-4 (1920).—The values given by Voigt (Göttinger Nachr., 1888) do not accord with the mol. theory of crystals. New values were detd. and checked by Richards' and Jones' compressibility data; they agree well with the theoretical value. J. ALEXANDER

Dissociation of halogen compounds. A. v. WEINBERG. *Z. Physik* 3, 337-42 (1920).—W. shows how it is possible, from thermal data and Born's calcs. for the dissociation work of crystal lattices, to calc. the heats of dissociation into atoms of gaseous metallic halides. F. C. HOYT

The theoretical determination of the equation for the vapor tension for any substance starting with the density and the coefficient of dilatation at a given temperature below the boiling point. I. Carbon. J. J. VAN LAAR. *Rec. trav. chim.* 39, 647-56 (1920).—v. L. states that the formula of v. Liempt (*Z. anorg. allgem. Chem.* 111, 280 (1920)) can be used for only a certain group of substances. He deduces one from his own general formula (*C. A.* 14, 3184) which in this paper is applied to C. The triple point of C or  $T_{tr} = \frac{1}{3}T_c$  or the critical temp. while the relation for the b. p. is  $T_c/T_r = 1.5$ . The calcd. and observed results indicate that approx.  $T_{tr} = 3900^\circ$ ,  $T_r = 5200^\circ$  and  $T_c = 7800^\circ$  (abs.). E. J. WITZEMANN

The value of "a" in van der Waals' equation and the nature of cohesion. ALBERT P. MATHEWS. Univ. Chicago. *Verhandel. Akad. Amsterdam* 12, No. 4, 1-77 (1917).—This monograph is a complete recapitulation and summary of the author's theories of cohesion as expressed in the formula  $a = N^2(m^2k \times Val/M)^{2/3}$ , where  $a$  is the van der Waal constant,  $N$  the no. of mols. in the vol. of gas or liquid for which  $a$  is computed,  $m$  the gravitational mass of the mol.,  $k$  is the gravitational constant,  $Val$  the no. of valences, and  $M$  the mol. wt. For the original papers cf. *C. A.* 6, 3040; 7, 1999, 2143, 2376, 3695; 8, 1893, 2830; 9, 400, 2940; 10, 3006. The direct purpose of this summary is to answer the objections to the theory and equation brought by van Laar (*C. A.* 10, 2059), and in turn to criticize the additivity principle of van Laar (*C. A.* 10, 2059). In addition new methods are included for computing  $a$ , and the dependence of cohesion both on gravitational and chem. attraction is pointed out.

G. L. CLARK

The problem of an equation of state. LEON SCHRAMES. *Z. Physik* 3, 255-61 (1920); cf. *C. A.* 14, 2881.—S. proves from thermodynamic principles and the assumption that the perfect gas laws hold at infinite dilution that there must be an equation of state of the form  $p + (a/v^2)v = RTf(v)$ , where  $a = \int_{-\infty}^{\tau} q d(1/T_v)$ . The integra-

tion is along an isochore, and  $q = -v^2 \frac{\partial \left( \frac{p}{T} \right)}{\partial \left( \frac{1}{T} \right)} v$ . From empirical data  $f(v) = v/(v-b)$ ,

as in van der Waal's equation. For the limiting case of  $p = \infty$ —the vol. is  $b$ , but for  $T = 0$  and  $p = 0$  the limiting volume is not the same for all substances.

F. C. HOYT

The chemical constant. G. HEIDHAUSEN. *Z. Elektrochem.* 27, 69-72 (1921).—The results of vapor pressure measurements by Egerton (cf. *C. A.* 11, 1582; 14, 666) with Zn and Cd have been employed to calc. the universal const.  $i_0$  in the theoretical relation,  $i = i_0 + 1.5M$ , derived by Tetrode (cf. *C. A.* 6, 2704). Here  $i$  is the chem. const. and  $M$  the mol. wt. of the gas. The values obtained for Zn and Cd, resp., are  $i_0 = -1.62$  and  $i_0 = -1.56$ . The mol. heat of vaporization of Zn and Cd at zero abs. is 31164 and 27275 cal., resp.

H. JERMAIN CREIGHTON

**Evaporation and stabilization of mercury droplets.** BARNET RIE. *Ann. Physik* 63, 759-85(1920).—From the diffusion theory of Stefans it is calcd. that mercury droplets of radius  $10^{-4}$  cm. rapidly distil into larger drops. The time of disappearance as calcd. is much shorter than the actual time found by Ehrenhaft (*C. A.* 10, 408) who worked with drops for as long as an hour without noticeable change in mass. The soln. of Pb or some other metal in the mercury droplets will reduce the vapor pressure, thus neutralizing the effect of increased vapor pressure due to the curvature of the surface of the droplet. Under these conditions the droplet will become very much more stable and may be worked with for longer periods. The discussion is entirely theoretical, no exptl. data being given.

C. R. PARK

**Color and the Brownian movement of ultramicroscopic particles.** REINHOLD FÜRTH. *Prag. Physik. Z.* 22, 80-7(1921); cf. *C. A.* 14, 436, 674; 15, 1240.—From observations of the color and the Brownian movement of a large number of ultramicroscopic particles of Au and Ag suspended in  $H_2O$ , the radii of the particles have been calcd. It has been found that the values for the radii when calcd. from the color ( $a_c$ ) differ from those calcd. from the Brownian movement ( $a_{br}$ ), in the sense  $a_{br} > a_c$  for Au and  $a_{br} < a_c$  for Ag. Possible causes of these deviations are discussed.

H. JERMAIN CREIGHTON

**Colloid development.** HARRY N. HOLMES. *J. Ind. Eng. Chem.* 13, 357-8(1921).—This rept. of accomplishments by the Committee on the Chemistry of Colloids contains a list of books on colloidal chemistry.

E. J. C.

**Viscosity and flocculation of coarse suspensions.** HANS EGNÉR. *Medd. K. Vetenskapsakad. Nobelinst.* 4, No. 4, 27 pp.—It is shown by viscosity measurements that no general formula for calcg. the viscosity of a suspension from its volume concn. is generally satisfactory. The properties of suspensions are shown to resemble closely those of suspension colloids. They are generally negatively charged and show characteristic electric endosmosis, cataphoresis, etc. Electrolytes have a great effect upon the state of these coarse suspensions. Cations flocculate and increase the viscosity and sedimentation height. Anions act in the opposite direction. With the exception of OH ions which act irregularly the magnitude of their flocculation power generally changes according to Hardy's law. (Cf. *C. A.* 14, 1918).

A. E. STERN

**The velocity of flocculation of selenium sol. I. Flocculation by potassium chloride.** H. R. KRUYT AND A. E. VAN ARKEL. van't Hoff Lab., Utrecht. *Rec. trav. chim.* 39, 656-71(1920).—Recent work indicates a relation between the stability of sols and the electrical charges carried by the dispersed particles so that all influences which diminish the charge diminish the stability. The influence best studied is the flocculating action of electrolytes. This process is composed of 2 parts and it may be asked (1) why the addition of an electrolyte discharges the particles, and (2) how are the discharged particles united to form the complexes. Freundlich has developed a useful theory in answer to the first question but the 2nd has not been so well studied. Smoluchowski (*C. A.* 11, 3140) developed a mathematical treatment of this subject and found that the variation of the no. of particles with the time  $t$  is given by (1)  $\Sigma v = v_0/[1 + (t/T)]$  and (2)  $\Sigma v = v_0/[(1 + e(t/T))]$ . If the relations are so simple one ought to find a new way of solving the problem of the elec. stability of sols. The expts. here described relate to the slow flocculation of Se sol (Svedberg and Philblad, *C. A.* 5, 404). The sol was prepd. thus: 90 cc. distd.  $H_2O$  are boiled with 5 cc.  $N_2H_4$  soln. (1.5 mol. per l.) to which 4 cc. of  $SeO_2$  soln. (0.1 mol. per l.) is added while boiling. When the color becomes dark yellow 1 cc. more of the latter is added. After cooling for 10 mins. this soln. is dild. to 400 cc. with  $H_2O$  condensed in a Ag condenser. The 2nd addition of  $SeO_2$  causes Se to ppt. on the Se already present and gives particles of the size desired (i. e., a no. varying from  $30 \times 10^6$  to  $40 \times 10^6$  per cc.). The  $SeO_2$

was obtained by dissolving pure Se in  $\text{HNO}_3$ , driving off excess  $\text{HNO}_3$  on the  $\text{H}_2\text{O}$ -bath and purifying by repeated sublimation. It is remarkable that  $\text{H}_2\text{O}$  distd. through Sn should give a more stable sol than that condensed in a Ag tube. The method used was similar to that used by Zsigmondy (*Z. physik. Chem.* 92, 600(1918)) in a similar study on the flocculation of Au sol. 1 cc. of the Se sol was dild. to a convenient concn. and the no. of particles in a detd. vol. was counted from time to time and was found to be unchanged after 3 or 4 weeks. Measured amts. were then mixed with a known amt. of the electrolyte and the change in the no. of particles was detd. The counting of particles was done with an ultramicroscope with a slit. The data obtained are given in tables. The results show that the addition of small amts. of KCl produces only a slow flocculation. When the concn. of KCl is raised the velocity of flocculation increases very rapidly and then becomes independent of all new additions. At still higher concns. there is a slight diminution in the velocity of flocculation (increase in  $T$ , the "Halbierungszeit"), showing that the particles again become charged. In calcg.  $T$  (or the time necessary for the reduction of the no. of particles by  $1/2$ ) from formula (1) it is found that the value is about const. in the region of very slow and fast flocculation but is highly variable in the intermediate region. Critical expts. are described which leave the conclusion unchanged that the course of the slow flocculation is different from that predicted on the basis of S.'s formulas. The rapid flocculation occurs essentially in conformity with formula (1) but with the slow flocculation  $T$  increases with the time so that the resemblance between the course of the 2 curves predicted by S. is not found. From the point of view of the relation between the velocity of flocculation and the concn. of the sol the agreement with S.'s theory also occurs in the case of the rapid flocculation, but in the case of the slow flocculation the phenomena are more complicated than this theory would lead one to suspect. E. J. WITZEMANN

Experiments on adsorption by metal powders. I. HANS V. EÜLER AND ARVID HJ. HJEDLUS. *Arkiv Kemi, Mineral. Geol.* 7, No. 31, 16 pp.(1920).—The author believes that the processes of adsorption, especially upon solid surfaces, are conditioned by the same chem. and elec. mol. forces which det. exchanges in homogeneous soln., rather than that they are to be explained upon the basis of surface tension. In other words, most adsorptions are cases of chem. reaction. An understanding of adsorption processes will be furthered best by the study of adsorptions in which the chem. process is clearly evident. Two such cases are presented in this paper: (1) the adsorption by Ag powder of  $\text{AgNO}_3$ , whose equil. with Ag from an electrochem. standpoint can be treated by the Nernst theory; and (2) the adsorption by Ag powder of KCl which leads to the formation of AgCl whose soly. is exactly known. The amt. of adsorption at several concns. was detd. by agitating 1 or 2 g. Ag powder with solns. of  $\text{AgNO}_3$  or KCl for 2 hrs., and then detg. the Ag or Cl concn. remaining in the soln. That the  $\text{NO}_3^-$  was adsorbed to the same extent as the  $\text{Ag}^+$  was shown by the facts that the soln. was not acid after adsorption, and that the percentage decrease of the elec. cond. of the soln. was approx. equal to the percentage of the total Ag which was adsorbed. From an approx. 0.1  $N$   $\text{AgNO}_3$  soln., 7.5% of the Ag was adsorbed by 1 g. Ag powder, and from a 0.0025  $N$  soln., 20% of the Ag. For 2 g. Ag powder the corresponding amts. were 15.6% and 27.3%. For KCl and 1 g. of Ag powder the amts. adsorbed were, for approx. 0.04  $N$  KCl, 6%; 0.02  $N$ , 7.3%; 0.01  $N$ , 10.6%; and 0.005  $N$ , 22.8%. By extrapolation, the max. amt. of adsorption on 1 g. Ag was 0.0007 g. mol. of Ag, and 0.001 g. mol. of Cl. The surface of 1 g. of the Ag powder used was estd. to be about 2 sq. meters. If the adsorbed layer is 1  $\text{Ag}^+$  deep, it is calcd. that the radius of the mol. sphere of influence of the  $\text{Ag}^+$  is  $0.7 \times 10^{-8}$  cm. The preparation of very finely divided pure Ag powder having particles of  $0.8\mu$ – $0.6\mu$  diam. is described. AgCl was reduced by Zn under  $\text{H}_2\text{O}$ . The Zn was removed by decanting 3–4 times with

10% NaOH soln., each decantation being followed by 3-4 decantations with distd.  $H_2O$ . The sepn. of the Zn by HOAc was tried, but it resulted in a discolored yellow product, and in the agglomeration of the Ag particles until their diam. reached  $10\mu$ . The purity of the Ag was tested by dissolving 1 g. in  $HNO_3$ ; the absence of turbidity showed the absence of Cl. The Ag was then pptd. as AgCl by NaCl, filtered, and washed.  $Na_2CO_3$  was added to the filtrate, and the absence of a turbidity of  $ZnCO_3$  after several hrs. standing showed the absence of Zn. The NaOH was removed by washing the Ag 10-20 times with  $H_2O$ . The Ag powder should be dried at room temp. Heating in an oven coarsens the particles. The AgCl used should be pptd. from a cold, neutral soln. otherwise the particles may be too large. Further experimental work, and the theoretical treatment of the results will appear later. R. H. L.

The adsorbing power of norite compared with that of blood charcoal. H. R. KRUYT and C. F. VAN DUIN. van't Hoff Lab., Utrecht. *Rec. trav. chim.* 39, 679-84 (1920).—In the course of work to be published K. and v. D. have detd. whether "norite" (manufd. by Agemeene Norit-Maatschappij at Amsterdam) is as good for adsorption investigations as Merck's blood charcoal purified with acid. This was done by detg. the adsorption isotherms of both materials for the OH-ion of NaOH, the H-ion of HCl, for PhOH (C. A. 8, 2289), for the anion of the acid Na  $\beta$ -sulfoacinnamate ( $a$ ) (Moore, *J. Am. Chem. Soc.* 25, 622(1903)) and for Br. The anion of  $a$  is detd. by detg. the addition of Br thus: excess of a soln. of bromate and bromide is added and then HCl; after 1 hr. KI is added and the free I titrated with  $Na_2S_2O_4$ . The norite used sometimes contained alkali. For this reason dry norite, of which 1 g. consumed 19.3 cc. 0.1  $N$  acid, was heated with excess dil. HCl, and washed with  $H_2O$  until neutral. This was called norite II and was used for the above detns. Norite I was also used for the last 3 detns. listed above. The results show that although norite gives regular isotherms of adsorption the value of  $1/n$  is less than with blood charcoal. It is suggested that this difference is due to the higher temp. at which norite is prepd. E. J. W.

Method of carrying out and following quantitatively chemical reactions with masses of the order of  $10^{-14}$  grams. D. K. KONSTANTINOWSKY. *Physik. Z.* 21, 689-90 (1920).—A particle of substance  $A$  is brought between the horizontal plates of a condenser. The particle has the mass  $m$ , and carries the charge  $e$ . If a field is set up of strength  $E$ , such that the particle is stationary,  $eE = mg$ . Since the field is proportional to the distance,  $V$ , between the plates of the condenser,  $m = kV$ . A gas with which the particle reacts is now brought between the plates. The distance between the plates is adjusted to the point where the particle is again stationary. Then  $m_1 = kV_1$ , where  $m_1$  is the mass of the reaction product and  $V_1$  the distance between the plates in the second case. From this it follows that  $m/m_1 = V/V_1$ . From the ratio of the distances between the plates is known the ratio of the masses of the starting substance and the reaction product. Measurements made in this way are accurate to within 1%. No data are given. C. R. PARK

Further light on the theory of the conductivity of solutions. A criticism of Kohlrausch's law. GUY CLINTON. Separate printed by the Chemical Publishing Co., Easton, Pa. 1921. 15 pages.—The criticism is adverse. JAMES M. BELL

Theory of electrolytic ions. XIV. The additive conductivity law of Kohlrausch. RICHARD LORENZ. Frankfurt a. M. *Z. anorg. allgem. Chem.* 111, 55-75(1920).—On the basis of the theory of complete ionization, of Bjerrum, an equation is developed by the aid of which may be calcd. the ion conds. at various concns. The change in cond. with diln. is ascribed to change in the mobility of the ion. The variation in transference numbers is due to disproportionate change in the mobilities of the two ions. The so-called cond. ratio,  $u/u_0$  is replaced by two independently varying quan-

ties,  $U/V_0$ , the mobility ratio of the cation, and  $V/V_0$ , the mobility ratio of the anion. These two ratios are calcd. for the  $\text{Na}^+$  ion, the  $\text{K}^+$  ion and the  $\text{Cl}^-$  ion, from a number of solns. for each ion. They show the source of variation in the transference numbers in  $\text{NaCl}$  soln. and explain the constancy of the transference number in the case of  $\text{KCl}$  where the mobilities of the  $\text{K}$  and  $\text{Cl}$  ions change at the same rate. All quantities are calcd. from the cond. data of Kohlrausch. No calcs. are made for concns. above 1  $N$ . XV. Volume ratio and mobility of univalent organic anions. *Ibid* 148-50; cf. *C. A.* 13, 2799.—The same quantities are calcd. as in the former article, this time for the anion. XVI. Conductivity of arsenic acids. RICHARD LORENZ AND ERIKA SCHMIDT. *Ibid* 175-92.—Cond. measurements are carried out on 15 addition products of the substance  $\text{C}_6\text{H}_5\text{AsO}(\text{OH})_2$ . From these measurements are calcd. mol. conds. at zero concn., degree of dissociation at the various concns., and the mass action const.

C. R. PARK

**Ionization of strong electrolytes.** WM. D. HARKINS. *Proc. Natl. Acad. Sci.* 6, 601-5(1920).—This note is concerned with the various ideas conveyed by the terms ion and ionization. The idea supported by many workers particularly in the field of physics that strong electrolytes are completely ionized in soln. is in the sense simply of a charged particle—not necessarily one which is free to move in an elec. field as connoted in the older meaning of ion—or in other words polar atoms such as those which make up the mol. of a gaseous salt or solid crystal. Thus if the terminology is such that the salt is considered 100% ionized in the solid or gaseous state, it would be absurd to say that it is less than 100% ionized in soln. However, many of the pairs of positive and negative polar particles are so close together that they are not free to move in an elec. field. These may then be called *bound ions*, while those far apart are *free ions*. A salt like  $\text{NaIO}_3$  may therefore be 100% polarized or ionized, 85% electrolytically dissociated and 68% thermodynamically dissociated—each a distinct feature. A distinction should be made between ionization in the sense of charged particles and in the sense of dissociation in cases of obvious sepn. of the polar particles. It follows that the exptl. method will det. what is meant by % dissociation, since with all degrees of separation it cannot be an absolutely definite thing. If the newer connotation of ionization is to be retained, complex and intermediate ions may be termed *ion associates*. However, it may be preferable to retain the older meaning and designate a gaseous salt mol. as made up of *polar atoms*.

G. L. CLARK

**The mobility of univalent organic ions.** C. v. HEVESY. Copenhagen. *Z. Elektrochem.* 27, 77-8(1921); cf. *C. A.* 15, 1241.—In the case of nearly all univalent org. ions, the mol.-ion (unhydrated ion) is so large, and the strength of the elec. field with which the ions act on the  $\text{H}_2\text{O}$  molcs. so correspondingly small, that the adding on of  $\text{H}_2\text{O}$  does not occur. It is shown that this is in agreement with the findings of Lorenz (cf. *C. A.* 13, 2799) with reference to the magnitude of univalent org. ions.

H. JERMAIN CRRIGHTON

**Freezing points of binary aqueous solutions of electrolytes.** OSKAR KLIRIN AND OLOF SVANBERG. *Medd. K. Vetenskapsakad. Nobelinst.* 4, No. 1, 13 pp.—The freezing points of aq. solns. of a large no. of binary mixts. of electrolytes were detd. Tables are given of  $\Delta$ , the freezing point lowering;  $\delta$ , the difference between  $\Delta$  and the sum of the f. p. lowerings of simple solns. of the constituent salts; and  $K$ , where  $K = \delta / C_1 C_2$ ,  $C_1$  and  $C_2$  being the concns. of the two electrolytes. There is no general rule concerning the sign of  $\delta$ ; in most cases it is positive. For mixts. of halogen acids and alkali halides  $K$  is positive and fairly const. but for alk. earth salts  $K$ , though mostly positive, increases with the concn.

A. E. STEARN

**The freezing point of wet benzene, and the influence of drying agents.** NEVIL VINCENT SIDGWICK. Oxford Univ. *J. Chem. Soc.* 117, 1340-3(1920).—The max.

depression of f. p. of carefully dried benzene by addition of water is  $0.100^\circ$ . This affords a convenient method for detg. the relative efficiency of various drying agents. If the wet benzene is shaken with a solid dehydrating agent, which is insol. in it, until a const. f. p. is obtained, the ratio of the depression observed in the presence of the drying agent to that produced by pure water is a measure of the lowering of the vapor pressure of the water by the latter, and hence of the efficiency of the drying agent. This efficiency must be the same (at temps. near  $5^\circ$ ) for a soln. in any solvent in which the drying agent is insol. Dehydrating agents investigated are given in ascending order of efficiency as follows:  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CuSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{NaOH}$  and  $\text{P}_2\text{O}_5$ . Removal of water by  $\text{P}_2\text{O}_5$  was apparently complete.

J. T. R. ANDREWS

**Hydration of the lithium cation.** J. BARBOROVSKÝ AND V. HANÁK. *Chem.-Listy* 15, 3-5(1921).—The authors detd. by a direct gravimetric method the increase in wt. of the soln. of  $\text{LiCl}$  at the cathode. The amts. of  $\text{LiCl}$  and water that were carried to the cathode by the elec. current were calcd. from the difference between the initial and final concns. of the cathode soln. These data allowed the authors to obtain the transport number of the  $\text{Li}^+$  and the amt. of water associated with the  $\text{Li}^+$ . Presupposing that  $\text{Cl}^-$  has no affinity for water, then the expt. indicated that 18 mols. of water is linked with the  $\text{Li}^+$ .

JOHN M. KRNO

**The size of the ions of the alkali metals.** RICHARD LORENZ. *Z. Physik* 2, 175-80 (1920).—L. tabulates values estd. by Born, Landé, Heydweiller, Wogan and Born and Lorenz, for the ions and the atoms of  $\text{Li}$ ,  $\text{Na}$ ,  $\text{K}$ ,  $\text{Rb}$ ,  $\text{Cs}$ , and compares them on the basis of the relation he has shown to exist between the space occupied and the activity of motion of ions. Born suggested that the values calcd. by him from the heat of hydration should be reduced by  $9.9 \times 10^{-8}$ , the diam. of a water mol. The corrected values agree remarkably with those calcd. by L.

JEROME ALEXANDER

**The velocity of transmigration of ions in crystals.** G. v. HEVESY. *Z. Physik* 2, 148-9(1920).—Applying the Einstein relation between diffusion and kinetic activity to est. from cond. data the velocity with which the ions of a crystal diffuse into the crystal itself, i. e., transmigrate, it is found that at room temp. the values obtained are vanishingly small. With rock salt the transmigration const. at  $20^\circ$  figures somewhat less than  $3 \times 10^{-18}$  cm.<sup>2</sup> per day; the value rises rapidly with temp., being 200 times greater at  $150^\circ$ ,  $1.4 \times 10^{-4}$  cm.<sup>2</sup> at  $626^\circ$ , and close to the m. p. reaching a value only 3000 times less than at the m. p. where a sharp rise occurs. With alkali nitrates this "preparation" for fusion begins later than with the chlorides, but the reverse is the case with heavy metal halides. With  $\text{PbCl}_2$  the transmigration const. figures: at room temp.  $8 \times 10^{-8}$  cm.<sup>2</sup>, and at  $30^\circ$  below the m. p. as low as  $2.7 \times 10^{-9}$  cm.<sup>2</sup>. This last value was detd. experimentally by following the diffusion of radioactive  $\text{PbCl}_2$  into inactive  $\text{PbCl}_2$ , the activity showing the degree of penetration. The valve found, 0.019 cm.<sup>2</sup>, agrees well with the one calcd. With mixed crystals the transmigration is more rapid, but only reaches appreciable values near the m. p.

JEROME ALEXANDER

**Theory of the speed of reactions in gases.** KARL F. HERZFELD. *Ann. Physik* 59, 635-67(1919).—Largely mathematical. The previous work of M. Trautz (*C. A.* 3, 2891) is discussed. With exothermic reactions where there is no bond or only one, every collision is effective, irrespective of the temp. On the other hand, where two bonds exist only a fractional portion of the collisions, depending on temp., are effective. With the only known case of an exothermic reaction (formation of  $\text{HBr}$ ) the result of a collision depends upon the kinetic energy (dependent upon speed of the encounter) which must exceed the heat of reaction. Hence with exothermic reactions the number of effective molecular encounters is governed by a thermodynamic factor depending

on the internal specific heat. The formulas developed agree well with the measurements of Bodenstein and Lind on the formation of  $\text{HBr}$ . JEROME ALEXANDER

**Rapid pyrogenic decomposition of formic acid and the preparation of carbon monoxide.** J. A. MÜLLER AND M. E. PEYTRAL. *Bull. soc. chim.* 29, 34-9 (1921). —The pyrogenic decompn. of  $\text{HCO}_2\text{H}$  yields principally  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$  vapor. Small quantities of  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$  and  $\text{CH}_4$  also are formed by direct reduction of some of the acid by the  $\text{H}_2$  liberated. While the  $\text{CO}_2$  and  $\text{H}_2$  evidently come from a primary decompn. of the acid according to the equation, (1)  $\text{HCO}_2\text{H} = \text{H}_2 + \text{CO}_2$ , the  $\text{H}_2\text{O}$  and  $\text{CO}$  may result either from another primary decompn. of the acid or from a secondary reaction of the products of (1). The authors have sought to establish whether the reaction, (2)  $\text{HCO}_2\text{H} = \text{H}_2\text{O} + \text{CO}$  or, (3)  $\text{H}_2 + \text{CO}_2 = \text{H}_2\text{O} + \text{CO}$  accounts for the formation of the  $\text{H}_2\text{O}$  and  $\text{CO}$ . The vapors of  $\text{HCO}_2\text{H}$  were passed rapidly through a Pt tube heated at  $1150^\circ$ . A series of 5 expts. were made, the rate of passage of the acid through the tube being varied. Assuming that the decompn. proceeds according to the first order reactions (1) and (2), then, neglecting the small quantities of hydrocarbons formed, there should have resulted equal vols. of  $\text{H}_2$  and  $\text{CO}_2$  on one hand and equal vols. of  $\text{H}_2\text{O}$  and  $\text{CO}$  on the other. Designating by  $x_1$  and  $x_2$ , resp., the ratios of the number of mg.-mols. of  $\text{CO}_2$  and of  $\text{CO}$  to the corresponding number of mg.-mols. of  $\text{HCO}_2\text{H}$ , the ratios of  $x_1/x_2$  should have been equal for each expt. regardless of the rate of passage of the acid through the tube. Such was not the case, however. In the 5 expts. carried out the values of  $x_1/x_2$  varied from 3.19 to 0.79, decreasing in direct proportion to  $n$ , the av. number of mg.-mols. of  $\text{HCO}_2\text{H}$  passing through the tube per sec. The conclusion is hence drawn that, in the thermal decompn. of  $\text{HCO}_2\text{H}$ , the  $\text{CO}$  results from a secondary reaction which must necessarily be (3). From the exptl. data, the velocity of reaction (1) was calcd. as 2.544. From this value,  $x$ , the decompn. coeff. of the reaction could be detd. and was found to agree very closely with the exptl. values. For the bimol. reaction (3), which is of the 2nd order, the following formula was derived:  $dx/dt = k/V(x - X)^2$  where  $X$  is the fraction of  $x$  which reacts according to (3) in the time  $t$ ,  $V$  is the mol. vol. of the system in this period and  $k$  the usual velocity const. It is noted that at sufficiently high pressures the velocity of reaction (3) may become very great and the  $\text{HCO}_2\text{H}$  would appear to decompose directly into  $\text{H}_2\text{O}$  and  $\text{CO}$ . From the fact that this sort of decompn. does not occur even at high temp., the theory is advanced that, in the prepn. of  $\text{CO}$  by the action of  $\text{HCO}_2\text{H}$  on  $\text{H}_2\text{SO}_4$ , the latter does not merely play the role of dehydrating agent but that it may act catalytically, first giving  $\text{H}_2\text{O}$  and  $\text{HCOHSO}_4$ . The  $\text{HCOHSO}_4$ , being unstable, is thought to decompose as fast as formed into  $\text{CO}$  and regenerated  $\text{H}_2\text{SO}_4$ . A. T. FRASCATI

**The pyrogenic decomposition at high temperature of benzene and benzaldehyde.** M. E. EGLANTINE PEYTRAL. *Bull. soc. chim.* 29, 44-7 (1921); cf. C. A. 14, 1115, and preceding abstract.—I. *Benzene*. The principal products formed in the pyrogenic decompn. of  $\text{C}_6\text{H}_6$  are  $(\text{C}_6\text{H}_5)_2$  and  $\text{H}_2$  according to the equation:  $2\text{C}_6\text{H}_6 = (\text{C}_6\text{H}_5)_2 + \text{H}_2$ . This affords another illustration of the rule that the decompn. will follow that reaction requiring the least possible deformation of the mol. The gaseous products, which consist of over 90%  $\text{H}_2$ , also contain varying quantities of  $\text{CH}_4$ , depending upon the rate of passage of the  $\text{C}_6\text{H}_6$  vapors through the tube. In view of the stability of the  $\text{C}_6\text{H}_6$  (less than 2% decomposes when the rate is not more than 0.5 g.-mol. per sec.), it is very probable that the  $(\text{C}_6\text{H}_5)_2$  undergoes a second decompn. which accounts for the  $\text{CH}_4$  together with some of the  $\text{H}_2$  and free C. II. *Benzaldehyde*. The decompn. products of  $\text{C}_6\text{H}_5\text{CHO}$  are  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{C}_6\text{H}_6$ ,  $(\text{C}_6\text{H}_5)_2$ ,  $\text{CH}_4$ , free C and small quantities of anthracene and  $\text{C}_2\text{H}_2$ . The main reactions involved are the following: (1)  $\text{C}_6\text{H}_5\text{CHO} = \text{CO} + \text{C}_6\text{H}_5$  and (2)  $2\text{C}_6\text{H}_5\text{CHO} = (\text{C}_6\text{H}_5)_2 + 2\text{CO} + \text{H}_2$ . The forma-



tion of anthracene is probably due to the condensation of 2 mols. of  $C_6H_5CHO$  in the presence of  $H_2$ , while the  $CH_4$  and free C may originate from a partial decompn. of the  $(C_6H_5)_2$ . By a method of calcn. similar to that used in the preceding expts., reactions (1) and (2) are detd. as being of the 1st order and the decompn. of  $(C_6H_5)_2$  as a 2nd order reaction.

A. T. FRASCATI

The pyrogenic decomposition at high temperature of allyl alcohol. MLLR. EGLANTINE PEYTRAL. *Bull. soc. chim.* 29, 39-44 (1921); cf. *C. A.* 14, 1115, and preceding abstracts.—When the vapors of rectified, com. allyl alc. are passed through the pyrogenic decompn. app. the main products of the decompn. are  $C_2H_4$ ,  $C_2H_2$ , CO,  $H_2$  and  $CH_4$ . Small quantities of  $CH_2:CHCHO$ ,  $C_3H_2$ ,  $C_3H_4$  and free C also are obtained. The principal reactions involved in the decompn. are: (1)  $CH_2:CHCH_2OH = CH_2:CHCHO + H_2$  and, (2)  $CH_2:CHCH_2OH = CH_2:C:CH_2 + H_2O$ . The acrolein of reaction (1) undergoes a secondary reaction: (3)  $CH_2:CHCHO = CO + CH_2:CH_2$ , while the allene of reaction (2) appears to be completely reduced to  $C_3H_4$  by the liberated  $H_2$  and is not present as such in the reaction products. Representing by  $x_1$  and  $x_2$ , resp., the mol. ratios of the sum of the acrolein and CO and of the  $C_3H_4$  to the alc. evapd., the values of  $x_1/x_2$  are obtained. These are found to be practically independent of  $n$ , the av. number of mols. of the alc. vapor traversing the tube per sec., showing reactions (1) and (2) to be of the 1st order. The coeff.  $x_1$  is about double  $x_2$ , indicating that for every 3 mols. of alc. decomposing 2 mols. do so according to (1). In other words, the principal decompn. is that which produces the least possible deformation of the mol., a rule which has been established in identical studies of similar compds. When  $v$ , the mol. ratio of the CO formed to the alc. evapd., is calcd., it is noted that  $v/x_1$  varies inversely as  $n$ . Since  $x_1$  is the coeff. of a 1st order reaction, the deduction is made that the formation of CO in the thermal decompn. of allyl alc. takes place according to reaction (3), which is of the 3rd order.

A. T. FRASCATI

Internal energy of inflammable mixtures of coal gas and air after explosion. W. T. DAVID. Univ. Coll. of S. Wales and Monmouthshire. *Proc. Roy. Soc. London* 98A, 303-18 (1921); cf. *C. A.* 14, 893, 3565.—The results of previous measurements of heat condensation and radiation from mixts. of coal gas and air (15.0, 12.4, and 9.7% coal gas) exploded in a cylindrical cast-iron vessel  $30 \times 30$  cm., are summarized in tables and curves. The rate of total heat loss per sq. cm. of wall surface per sec. ( $H$ ) in a cylindrical vessel / cm. by / cm. containing mixts. of coal gas and air is given approx. by  $H = 4 \times 10^{-13}(T - T_w)^4 + 0.32 \times 10^{-14}T^{1/2}$  above  $2000^\circ$  abs. and  $H = 7 \times 10^{-16}(T - T_w)^2 + 0.32 \times 10^{-14}T^{1/2}$  below  $2000^\circ$  abs.  $T$  = temp. of gaseous mixt. and  $T_w$  = temp. of walls of explosion vessel. The heat loss measurements were applied to the estn. of the internal energy and the volumetric heat of the different mixts. at various temps. after explosion. The internal energy and volumetric-heat curves so obtained indicated that at the moment of max. pressure about 10% of the heat of combustion of the coal gas in each mixt. has not been converted into thermal energy, and that after-burning continues for at least 0.25 sec. after max. pressure has been attained. It is believed that these results show that the energy of combustion of the coal gas originally in the vessel is distributed at the moment of max. temp. as follows: (1) Internal (thermal) energy: From about 72% of the heat of combustion of the coal gas in a 9.7% mixt. to about 80% in a 15% mixt. (2) Available chem. energy: About 10% in each mixt. (3) Heat loss to the walls of the vessel: From about 10% in a 15% mixt. to about 18% in a 9.7% mixt.

D. MACRAE

Experimental investigation of the kindling temperature and the reaction velocity of the hydrogen-oxygen mixture. HERMAN FISSEL. *Z. physik. Chem.* 97, 158-78 (1921).—Kindling temp. is defined and its practical meaning indicated. Detns. have been made of the kindling temp. of H-O mixts. containing different proportions of

these gases. Approx. detns. also have been made of the kindling temp. of  $C_2H_2$ -air mixts. The lowest kindling temp. ( $397.5^\circ$ ) found for H-O mixts. was obtained with a mixt. consisting of  $3H_2 + 2O_2$ . Values of the velocity coeff. of the reaction  $2H_2 + O_2 = 2H_2O$  have been detd. with a limited degree of accuracy. These values vary from  $3.07 \times 10^{13}$  at  $412.1^\circ$  to  $1.46 \times 10^{16}$  at  $539.3^\circ$ . The reaction between moist H and O is bimol., or proceeds with the intermediate formation of  $H_2O_2$ , while that between dry H and O is trimol. It is probable, although not yet certain, that the "apparent" catalytic action of  $H_2O$  vapor depends merely on a concn. change of the mixt. This conclusion is based on the fact that if the concn. is changed through the admixture of portions of indifferent gas, then in accordance with the law of mass action the velocity of the reaction must decrease, the velocity const. having a definite value for each temp. In consequence the kindling temp., which depends upon the reaction velocity, will be raised. The possibility of detg. the heat of formation of  $H_2O_2$  in the gaseous state with the app. employed in the investigation, provided only this substance is formed, is discussed. It is pointed out that still more exact values for the velocity constns. could be obtained if the reaction could be carried out at const. vol. and a method of pressure measurement devised which resulted in no kinetic or frictional losses.

H. JERMAIN CREIGHTON

A theory of chemical reactivity. Calculation of rates of reactions and equilibrium constants. SAUL DUSHMAN. *J. Am. Chem. Soc.* 43, 397-433 (1921).—A theory of unimolecular reaction velocities is suggested according to which the velocity constant

$$\frac{Q}{-RT}$$

is given by the relation, based on the quantum theory,  $k_1 = (Q/Nh)e$ , where  $Q$  denotes the heat of activation, and  $N$  and  $R$  have the usual signification. The heat of activation also can be calcd. from the temp. coeff. of  $K_1$  by van't Hoff's equation. A comparison of the two methods in the case of the dissociation of phosphine gives very satisfactory agreement. As shown by Trautz and others, the velocity const.,  $k_2$ , of a bimolecular reaction in gases can be calcd. from considerations based on the kinetic theory of gases. Since the equil. const.  $K$  of any reaction is given by the value of  $k_1/k_2$  it follows from the above theory that, for any homogeneous gas reaction, it ought to be possible to calc. the free energy from data on the total energy of the reaction, or *vice versa*. In other words, this theory leads to a relation which is similar in certain respects to that derived by Nernst on the basis of his heat theorem. Working over the available data on homogeneous gas reactions, it is shown that the agreement between values of the heat reaction calcd. from equil. constns. by means of the above theory are in fair accord, in a large percentage of the cases, with the total heats actually observed. The results also show that the relation suggested for unimolecular reaction velocities can be regarded, at present, as only approx. true.

SAUL DUSHMAN

Fractional precipitation. PIERRE JOLIBOIS, ROBERT BOSSUET AND CHEVRY. *Compt. rend.* 172, 373-5 (1921); cf. *C. A.* 14, 657.—NaOH added to a mixt. of Ag and Cu nitrates in soln. ppts. the Cu completely as oxide before any of the Ag is deposited. The sepn. is quite distinct. In the case of a mixt. of the chlorides of Ni and Co the fractionation by NaOH is imperfect, the ppt. is always richer in Ni than it would be were the partition of precipitant equal, and the supernatant liquid shows a higher ratio of Ni to Co when the pptg. liquid is increased in NaOH concn. It is improbable that basic salts are formed in this reaction, since the quantities of metal remaining in soln. decrease proportionally as NaOH soln. is introduced.

J. T. R. ANDREWS

The separation of two salts having a common ion. A. TH. SCHLOSING. *Compt. rend.* 171, 977-81 (1920).—This practical procedure for the sepn. of 2 salts, A and B, having a common ion, is based upon the use of 4 exptly. detd. curves. Each of these

curves has temps. as abscissas, and the ordinates are: (1) and (2), the wt. of *A* and the wt. of *B* in 1 kg. of soln. satd. with respect to both salts, at different temps.; (3) the ratio of the ordinates of the above 2 curves; and (4) the wt. of  $H_2O$  in 1 kg. of the satd. soln. Suppose it were desired to sep. the pure salt *A* from a soln. containing *A* and *B*. First analyze the soln. Then conc. the soln. at a high temp. until a soln. satd. with respect to the 2 salts is obtained. The wt. of  $H_2O$  which must be distd. off to accomplish this, or the decrease in wt. of the soln. is to be calcd. from the curves. This concn. of the solns. will be accompanied by the partial sepn. of one of the salts which is removed. The satd. soln. obtained at the higher temp. is then to be cooled to a lower temp., after the addition to it of the wt. of  $H_2O$  calcd. to be sufficient to keep all of *B* in soln., whereupon the pure salt *A* will partly sep. out. The method of calcg. from the curves the wts. of  $H_2O$  to be added, the yield of salt to be expected, and the optimum temps. at which to work is detailed. This method was used for the separation of  $NH_4NO_3$  from  $NaNO_3$ , which is necessary in the manuf. of  $NH_4NO_3$  from  $NH_4HCO_3$  and  $NaNO_3$ . Data are given for the curves which were used in this case. R. H. L.

Cation catalysis. IV. BROR HOLMBERG. Stockholm. *Z. physik. Chem.* 97, 134-57(1921); cf. *C. A.* 8, 285.—It is suggested that cation catalysis in reactions between two strong electrolytes MAR and MB depends on the fact that the substance MAR, in which the reacting radical constitutes but a portion of the anion, reacts more rapidly when undissociated than in ionic condition; while, on the other hand, the electrolyte MB, in which the anion is identical with the negatively charged reacting radical, reacts in both the mol. and ionic conditions with practically the same velocity. It has been found that  $C = C_1\alpha + C_m(1 - \alpha)$ , where  $\alpha$  is the degree of dissociation of the electrolyte MAR,  $C$  is the velocity const. of the reaction between MAR and MB,  $C_1$  is the velocity const. of there action between  $(B^- + MB)$  and the  $AR^-$  ion, and  $C_m$  is the velocity const. of the reaction between  $(B^- + MB)$  and the MAR mols.—In order to test these hypotheses, the reaction velocity of the action of several thiocyanates on  $CH_3IClO_3H$  has been detd. in neutral and acid solns. at 25°. With a const. K concn., velocity const. of the 2nd order have been obtained for the reaction,  $CH_3IClO_3K + KSCN = KI + CH_3(SCN)CO_2K$ . These const. are independent of the initial concns. of the reacting substances, and depend only on the total K concn. With an increasing K concn.,  $[K]$ , the value of the velocity const.,  $C$ , increases, the relation between these 2 quantities being given approx. by the expression,  $C = 2.60[K]^{0.157}$ . Values for  $C$  calcd. by means of the equation  $C = C_1\alpha + C_m(1 - \alpha)$  were found to be in complete agreement with those detd. by expt., when the values  $C_1 = 1.12$ , and  $C_m = 4.19$  were employed, and when the dissociation const. of the 1st electrolyte was  $k = 0.4$ . For Na salts  $C = 2.46[Na]^{0.17} = 1.12\alpha + 4.25(1 - \alpha)$ , when  $k = 0.4$ ; while for  $NH_4$  salts  $C = 2.66[NH_4]^{0.167} = 1.12\alpha + 5.16(1 - \alpha)$ , when  $k = 0.4$ . For Ba salts  $C = 3.12[Ba]^{0.161}$ . In solns. made markedly acid by the addition of HCl, the velocity const. is independent of the initial concns. and of the concns. and kind of metal present. For the reaction between undissociated  $CH_3IClO_3H$  and thiocyanate in any form, it has been found that  $C_m(\text{acid}) = 5.72$ . Although for free  $CH_3IClO_3H$ , in the absence of HCl, the velocity const. is also independent of the concn. and kind of metal present, it increases with increase in the initial concn. of the acid. Values calcd. for this velocity const. with  $C_1 = 1.12$ ,  $C_m = 5.72$  and the degree of dissociation of the acid, by means of the equation given above, are about 2% smaller than those detd. by expt. This difference is due to the fact that the resulting  $CH_3(SCN)CO_2H$  is stronger than the  $CH_3IClO_3H$ , and in consequence the degree of dissociation of the latter acid is depressed, thus increasing the velocity of the reaction. On the whole, the assumptions that have been made are confirmed by the exptl. results.

H. JERMAIN CREIGHTON

The influence of copper on the rate of solution of iron in acids. **FREDERICK K. BELL AND WALTER A. PATRICK.** *J. Am. Chem. Soc.* 43, 452-65(1921).—Iron alloys containing from 0.1 to 5% Cu dissolve more slowly in 28.7% HCl at 20° than do pure electrolytic or reduced Fe. Pt and Ag in contact with pure Fe do not decrease the speed of soln., whereas Cu does. Expts. with 57% H<sub>2</sub>SO<sub>4</sub> were unsatisfactory. The explanation suggested for the action of Cu is that the Cu first dissolved is pptd. in a fine state at the surface of the Fe, where it oscillates between soln. and pptn.

JEROME ALEXANDER

Double decomposition in solutions of mixed salts and its graphical representation. **HENRY LE CHATELIER.** *Compt. rend.* 172, 345-50(1921).—For the geometrical representation of similar systems van't Hoff employed as coördinate axes the four edges diverging from the same corner of an octahedron, thus constructing in space a figure whose orthogonal projections were shown on two mutually perpendicular planes. The compn. of a mixt. of four salts in equil. may be represented with greater facility by plotting the acid ions as ordinates and the metallic ions as abscissae upon a system of axes forming a closed square. The concn. of the soln. at any point within the axes is plotted upon a perpendicular to the plane of the square in terms of gram mols. of the mixt. dissolved in 100 g. of water. By suitable constructions and interpretations many varied problems of salt solns. may be solved graphically, e. g., detn. of mixt. of three salts of compn. identical with that of the mixt. under consideration; surfaces of satn.; progress of crystn.; quantity of salt deposited; and the point at which one of the salts will begin to re-dissolve, a fact recently discovered by M. Rengade (*C. A.* 15, 1245 and here represented graphically for the first time. J. T. R. ANDREWS

Passivity of metals. **W. HUGHES.** *Nature* 106, 892-3(1921).—Passivity is considered to be due to a layer of HNO<sub>3</sub> or NO<sub>3</sub><sup>-</sup> ions adhering to any metal which is rendered passive by strong HNO<sub>3</sub>. The following picture of effects at the surface between Fe and dil. HNO<sub>3</sub> is given: On the metal side of the surface is a double electrolytic layer consisting of the positive ions of the metal and their valency electrons. On the liquid side are polarized mols. in regular surface lattice formation. HNO<sub>3</sub> is ionized but H<sub>2</sub>O is not. The NO<sub>3</sub><sup>-</sup> ions and the H<sub>2</sub>O mols. are attracted to respective Fe ions, resulting in the setting up of an e. m. f. in the metal. If this is large enough one of the metal ions will be discharged into the liquid momentarily as Fe(NO<sub>3</sub>)<sub>n</sub>, water will be formed from the H ions of the acid and any OH ions from the H<sub>2</sub>O, and the remaining H ion is momentarily liberated, a current of electricity being the result. Passivity on the other hand occurs when there is low potential and when the layer in the liquid above the surface is homogeneous, such as would be the case with strong HNO<sub>3</sub>. Activation by scratching, touching with a more electropositive metal, placing in a magnetic field or heating is easily explained upon the basis of the disturbance of such a homogeneous layer. G. L. CLARK

Heat of dissociation of iron pyrites. **H. KAMURA.** *Chem. Met. Eng.* 24, 437 (1921).—K. measured decompn. pressures at which S vapors are given off by FeS<sub>2</sub> at different temps., whereby he found the decompn. pressure curve and thence deduced thermodynamically the heat absorbed in the decompn. Exptl. results are plotted and the formula deduced is:  $\log p = -(8145/T) + 1150$ . K. writes the value of the heat expressed thermochemically as (FeS, S gas) = 18611 cal. W. H. BOYNTON

The significance of velocity constants with respect to the quantum theory. **MAX TRAUTZ.** *Z. Physik* 2, 117-28(1920).—Mainly mathematical. Velocity constants consist of two different factors, one expressing the possibilities of the reaction, the other giving the actual occurrence of the possibilities. The latter factor may be called the yield or activation factor. The former, which is the collision or oscillation figure, is mainly considered in this paper. JEROME ALEXANDER

The relation between some quantities in the equilibrium between carbonic acid and calcium carbonate. A. MASSINK. *Pharm. Weekblad* 57, 862-6(1920).—From the relations  $[H^+] = [CO_2]/[HCO_3^-] \times K_1$  and  $[H^+] = [HCO_3^-]/[CO_3^{--}] \times K_2$  and the soly. product of  $CaCO_3$ ,  $131 \times 10^{-10}$ , is obtained the equation  $[H^+] = 2.29 \times 10^{-3}[HCO_3^-]^2$  (1) if the value  $[CO_2] = [HCO_3^-]^2/(132.8 \times 10^{-4})$  is used, or  $[H^+] = 2.07 \times 10^{-3}[HCO_3^-]^2$  (2) if the value obtained by Auerbach from Tillman's data,  $[CO_2] = [HCO_3^-]^2/(162.3 \times 10^{-4})$  is used. A table is given showing the corresponding values of  $HCO_3^-$  in mg. per l. and  $p_H$  calcd. from (1) and also from (2). A curve is given in which  $p_H$  is plotted against cc. 0.1 N HCl used in detg.  $HCO_3^-$  above in 100 cc. water.

E. H.

Thermodynamics of mixtures. V. MARIO BASTO WAGNER. Lisbon. *Z. physik. Chem.* 97, 229-52(1921); cf. *C. A.* 15, 790.—A theoretical and mathematical paper in which the following topics are treated: methods for the detn. of the normality of pure substances; methods for the measurement of temp., vol., vapor pressure and the lowering of the f. p.; derivation of equil. conditions; the reversibility condition with reference to the exchange of a substance between 2 phases; the reversibility condition with reference to chem. reactions within a phase; ideal phys. mixts.; the Dolezalek theory in the light of experience.

H. JERMAIN CREIGHTON

The laws of energy and the cosmogonic process. ALFRED SCHACK. *Physik. Z.* 22, 73-5(1921).—A mathematical paper in which the question of the applicability of the 2nd law of thermodynamics to microcosmic processes is considered.

H. JERMAIN CREIGHTON

The mechanism of exchanges of energy during vaporization. RENÉ AUDUBERT. *Compt. rend.* 172, 375-8(1921).—The vaporization of a liquid involves the transference of a certain quantity of energy which is represented by the heat of vaporization. This last can be given a particular signification by considering it analogous to the disaggregation of a solid or of a liquid to the state of a dispersed phase, such as a suspension, emulsion, or colloidal soln. This analogy permits the latent heat of vaporization to be considered as a work effected against the forces of cohesion. Theoretical elaboration of this idea leads to a formula for calcg. the diam. of the mol., to a theoretical deduction of Trouton's rule, and verification of the relationship between the abs. b. p. and critical temp.,  $T_o/T_c = 2/3$ , as previously discovered by Guldberg. A. concludes that vaporization is a discontinuous phenomenon in which the elementary quantity of energy involved is equal approx. to  $10 \times 10^{-16} T_o$  ergs.

J. T. R. ANDREWS

Explanation of the electric phenomena in the decomposition of ammonium amalgam. GERTRUD ARONHEIM. Göttingen. *Z. physik. Chem.* 97, 95-133(1921).—A description is given of the methods and app. by means of which the elec. phenomena occurring during the decompn. of  $NH_4$  amalgam have been followed quant. Comparison of the regularities observed with those exhibited by gases bubbled through Hg points to the Lenard effect as the explanation of the  $NH_4$ -effect, i. e., as proceeding from the elec. excitation which gases produce when bubbled through liquids. While in the decompn. of  $NH_4$  amalgam the breaking of the gas through the bright surface of the Hg cannot be detected microscopically, this is doubtless due to the extremely finely divided state of the gas.

H. JERMAIN CREIGHTON

Utility of desiccants in electrostatic measurements. V. H. JACKSON AND A. T. MUKERJEE. *J. Proc. Asiatic Soc. Bengal* 16, 1-11(1920).—A Dolezalek electrometer and insulators were enclosed in an air-tight case and the rate of electrical leakage was measured when the initial charge was one v. The effect of drying the app. with  $CaCl_2$ , metallic Ba,  $P_2O_5$ ,  $CaO$ , and  $H_2SO_4$  was studied. The maximum allowable leakage is placed at 0.1 v. per minute. This value is exceeded in the presence of all the substances but  $H_2SO_4$ , which is therefore the best drying agent for electrostatic measurements.

C. R. PARK

**Abnormal behavior of a Weston standard cell.** M. G. MELLON. *Chem. Met. Eng.* 24, 166(1921).—Certain cells in the course of time develop abnormal characteristics. In the cell studied the e. m. f. was 0.001 v. low. Comparison with other cells should precede the use of any individual as a standard of reference. C. R. PARK

**Electrical resistance of metals.** P. W. BRIDGMAN. *Phys. Rev.* 17, 161-94(1921).—The variation of resistance with pressure and temp. has been observed in 18 elements. These data are briefly summarized and will be published elsewhere. The theory of *electronic conduction* advanced by B. (cf. C. A. 11, 1591) is elaborated and applied to the explanation of certain phenomena such as Ohm's law, the abnormally high resistance of alloys which form mixed crystals, the greater cond. of the phase occupying the smaller vol., etc. The material is dealt with in detail. C. R. PARK

**Further measurements of the effect of pressure on resistance.** P. W. BRIDGMAN. *Proc. Nat. Acad. Sci.* 6, 505-8(1920).—The present results supplement earlier values (C. A. 11, 748). In all six cases (Li, Na, K, Hg, Ga, Bi) the ratio of the elec. resistance of the element in the solid state to that in the liquid state varies but little, even with great increase in pressure. It also seems to be universally true that the temp. coeff. of the liquid is less than that of the solid, and the change of resistance on melting is in the direction of the change in vol. The following had negative pressure coeffs. of resistance: Na, K, Mg, Hg, Ga, Ti, Zr, As, W, La, Nd, Si, and black P. The coeff. is very small for Zr and Ti, resembling that for chromel. Na and K show decreases of 40% and 70% in resistance under 12,000 kg. pressure. The metals Li, Ca and Sr have positive coeffs. although all are highly compressible. JAMES M. BELL.

**The relation between electrokinetic potential pressure and the electric force at phase interfaces.** H. FREUNDLICH AND P. RONA. *Sitzb. preuss. Akad.* 1920, 397-402.—From two series of expts., the first detns. of current potentials in glass capillaries, the second detns. of interphase potential differences with the same glass after the method of Haber and Klemensiewicz, the authors conclude that the thermodynamic potential difference of Nernst,  $\epsilon$ , is by no means identical with the electrokinetic potential difference of Helmholtz,  $\zeta$ .  $\epsilon$  represents the p. d. between the interior of the first phase and that of the second phase, whereas  $\zeta$  represents the p. d. existing in movable fluid films, the exterior fluid with  $\zeta$  being activated not against the glass but against a firm liquid film adhering to the glass. In general an electrolyte concn. of 10 to 100 micromols (millionths mol.) will reduce the  $\zeta$  of pure water fractionally, and with 1000 micromols the p. d. vanishes. The cations are mainly responsible, that is their valence and other properties which are connected with their adsorbility. Least active are salts with univalent cations (NaCl, KCl); salts with bivalent cations are much more active, as also are acids. But none of these can change the negative charge of the glass to a positive charge; this transformation is effected by 1 to 2 micromols of  $\text{AlCl}_3$  (0.15 mg. per liter), and also by crystal violet. Since the electrokinetic double layer  $\zeta$  lies entirely in the fluid, the authors agree with Pellat and Perrin (*J. chim. phys.* 2, 601(1904)) in contradistinction to Helmholtz, that with dielectric constants, the fluid cannot be left out of consideration. JEROME ALEXANDER

**The thermochemical data of cadmium chloride and iodide.** HUGH S. TAYLOR AND GEO. ST. JOHN PERROTT. *J. Am. Chem. Soc.* 43, 484-93(1921).—The e. m. f.'s and the temp. coeffs. of 4 cells were studied, namely, Cd amalgam vs.  $\text{AgCl}$ ,  $\text{AgI}$ ,  $\text{PbCl}_2$ ,  $\text{PbI}_2$ , with Cd salt as electrolyte. Comparisons with other work indicate a precision better than 0.5 mv., and also indicate a disturbance of 4 or 5 m. v. when KI, "a substance foreign to the reaction under observation," is used as electrolyte. Calcd. values of the heats of combination indicate that the heat of formation of  $\text{CdCl}_2$  is 93,800 cal., not 93,240 (Thomsen). A direct calorific detn. agrees to 60 cal. with one result derived from cell e. m. f.'s for the heat of formation of  $\text{CdI}_2$ , 48,500 cal. W. P. WHITE

Thermal and electrical conductivity of lithium between 20 and 3730°K. **WALTHER MEISSNER.** *Z. Physik* 2, 373-9(1920).—M. measures for two different currents through a Li wire the resistances  $R$  and  $R'$  and the voltage drops  $E$  and  $E'$  between two points kept at const. temp.  $T$ . From this and Diesselhorst's relation  $\lambda/\kappa = (1/16R)(dR/dT)\{(E'^2 - E^2)/[(R' - R)/R]\}$  (cf. M. C. A. 10, 417) the thermal cond.  $\kappa$  and the elec. cond.  $\lambda$  are found.  $\lambda$  is nearly const. from 0 to 100° but falls off below 0°. Lorentz' relation  $\lambda/\kappa T = \text{const.}$  is not fulfilled. Abs. values of  $\lambda$  and  $\kappa$  are to be given later, provide purer Li can be prepd. **F. C. HÖRR**

The existence of equidistant layers normal to the optic axis in anisotropic liquids (liquid crystals). **F. GRANDJEAN.** *Compt. rend.* 172, 71-4(1921).—The reflection colors obtained from these liquids are due to parallel layers  $2 \times 10^{-4}$  cm. thick which are normal to the optic axis. **CHESTER B. SLAWSON**

Physical properties of thin metallic films. I. Magneto-resistance effects in thin films of bismuth. **J. A. BECKER AND L. F. CURTIS.** *Phys. Rev.* 15, 457-64(1920).—Following an historical sketch are results of expts. made on films of Bi deposited on glass by cathodic spluttering. These films showed initially no change in resistance in a magnetic field of 16 kg., but on heating to a temp. near the m. p. of Bi, variation (characteristic of cryst. Bi) was partially restored, photomicrographs showing a resultant recrystn. The original films showed a negative temp. coeff. of about 0.001 to 0.003 ohms per ohm per °C., this coeff. decreasing with temp. At about 240° the resistance begins to decrease rapidly until the film melts at 280°. II. Magneto-resistance effects in films of bismuth. **F. K. RICHTMYER AND L. F. CURTIS.** *Ibid* 465-75.—More exact quant. expts. continuing the work of part I. Films overheated during spluttering naturally show no inhibition of magneto-resistance variation; but such overheating produces no observable change in the negative temp. coeff. of resistance of the films. **JEROME ALEXANDER**

The "normal" concept and the statistical representation of results from chemical investigations. **HANS WOLFF.** *Chem.-Ztg.* 45, 109-10(1921).—The term "normal" is used with widely varying meanings, as shown by such terms as normal benzene, normal soln., normal temp., normal flask, normal value (statistical results), etc. In reporting statistical results the av. value, even when accompanied by maximum and minimum results, fails to tell the distribution of such values, and is less desirable, therefore, than a "distribution function" based upon grouping results in classes occurring throughout certain selected intervals, and then detg. in which group or groups the maximum number of results lies. This "peak value" is of great assistance in differentiating "normal" from "abnormal" values, as in comparing physical or chem. consts. of oils, foodstuffs, etc. In cases where the distribution curve is very irregular, it is better to plot a summation curve, det. the central position on the curve, and so learn the value above and below which the sums of the observed values equal one another. A compilation of 315 albumin detns. in milk analyses when so studied gave av. = 3.4%, peak value = 3.2 to 3.4% (15.5%), central value (from summation) = 3.1%, minimum = 1.98%, and max. = 6.71%. Inspection of the summation curve shows marked changes in slope at 2.4 and 3.8%, and that 239 results (76% of total) occur within these limits. The probability of finding albumin detns. within these limits is, therefore, three times as great as it is of finding values beyond them. "Abnormal" values thus become those whose frequency of occurrence is relatively small. "Normal" is not a fixed concept, and is incapable of exact definition. **W. C. EBAUGH**

Note on partial and total immersion thermometers. **C. W. WADNER AND E. F. MUELLER.** *J. Ind. Eng. Chem.* 13, 237-40(1921).—At 300° the error, due to emergent stem, of a thermometer calibrated to be read at partial immersion, is not likely to

exceed 1°. With partial immersion of a total immersion thermometer the error at 300° is likely to be 12°. A correction for emergent stem with a total immersion thermometer might easily leave an error of 1°. By proceeding to lower temps. the partial immersion thermometer gains more. Gradations finer than 1° are of little use with any thermometers when used with a long emergent column.

W. P. WHITE

**Inorganic phenomena of growth.** J. WINKELMANN. *Mikrokosmos* 14, 74-7 (1920-1).—A popular summary with a good bibliography. Phenomena of growth may occur in crystals, crystalloids, colloids, and amorphous ppts., and may be produced by intra-atomic and intramolecular forces, structure of the atoms and of the mol., and certain external influences such as diffusion, osmosis, internal friction of liquids, cohesion, adhesion, surface tension, and periodicity of pptn.

JOSEPH S. HEPBURN

**Recent advances in science—meteorology.** E. V. NEWNHAM. Air Ministry, London. *Sci. Progress* 15, 362-7(1921).—Review, with a section on the structure of the atm. when rain is falling.

JOSEPH S. HEPBURN

**Chart of viscosities in different systems.** H. G. NEVITT. *Chem. Met. Eng.* 22, 1171(1920).—The chart enables one to convert Saybolt, Redwood, Engler and abs. viscosities into each other quickly and accurately provided that the sp. gr. is known either on the abs. or B $\acute{e}$ . scales. The chart has a range from 1 centipoise, *i. e.*, viscosity of water at 20°, to 1100 cp.

EUGENE C. BINGHAM

**Some constituents of volatile oils and their structural relations.** INGO W. D. HACKH. *J. Am. Pharm. Assoc.* 9, 948-58(1920).—A new system of *org. chem. nomenclature*. The fundamentals consist of points and lines instead of the usual CHON symbols.

L. E. WARREN

**The adsorption capacity of various charcoals (HÖRST) 11A.** The settling of precipitates (DIETZ) 28. Oxidation and luminescence of phosphorus (WEISER, GARRISON) 3. Apparatus for ultra-filtration (VILLEGAS) 1. The affinity of the aragonite-calcite transformation (BÄCKSTRÖM) 8.

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OTTO, PAUL: Technischer Literatur-Kalender. 2nd Ed. Munich and Berlin: R. Oldenbourg. Bound M. 40. For review see *Feuerungstechnik*. 9, 9(1920).

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### 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

GERALD L. WENDT

**The atom model of Rutherford and Bohr in chemistry.** A. E. LACOMBLÉ. *Chem. Weekblad* 16, 832-4(1919).—A discussion of various difficulties which arise in the further development of the ideas suggested by Büchner (*C. A.* 13, 1710) in his application of the Rutherford-Bohr theories of at. structure to the case of atom linking in



org. compds. If the single bond between 2 C atoms be constituted by the attraction of 2 valency electrons revolving in an orbit perpendicular to the line joining the 2 positive nuclei, then, in addition to the electrostatic field, an electromagnetic field is established the direction of which is detd. by the sense of the motion of the electrons in the orbit. In the case of the methane mol. there would thus be several possible isomerides owing to the possibility of positive or negative rotation of the electrons in the 4 at. bonds as viewed from the C nucleus. Two of these isomerides are symmetrical, the rotations in one being all positive and in the other all negative. These are enantiomorphous isomerides, and each gives rise to one deriv. of the formula  $\text{CH}_3\text{R}$  and one  $\text{CH}_2\text{R}_2$ . The unsymmetrical possibilities may be represented as  $+++$ ,  $++-$ ,  $+-$ ,  $---$ . Each of these gives 2 isomeric mono-derivs. of the formula  $\text{CH}_3\text{R}$ . As these are unknown, it may be assumed that only the symmetrical forms exist. In chains of C atoms "positive" C atoms must alternate with "negative" atoms, so that a closed ring is possible only with an even number of atoms, unless for the odd atoms an abnormal structure is assumed, which would again render possible the existence of unknown isomerides. It is also pointed out that the displacement of the electrons to form orbits between the C atoms of the diamond would probably be indicated in the Röntgen diagram of the crystal by the presence of lines. Such lines have not been observed.

J. C. S.

Bohr's atom model and the theory of relativity. K. FÖRSTERLING. Danzig. *Z. Physik* 3, 404-7 (1920).—From Bohr's frequency condition  $E = h\nu$ , if  $h$  is a universal const. the shift in spectral lines can be derived from the changes in  $E$ . Thus for the transverse Doppler effect of special relativity  $\nu' = \nu/\sqrt{1 - (v^2/c^2)}$  as this is the ratio of the energies. For the difference predicted by general relativity for a system in a gravitational field (potential =  $\Phi$ ) and one where  $\Phi = 0$ , we have  $E' = E E[1 + (\Phi/c^2)]$  and hence  $\nu' = \nu[1 + (\Phi/c^2)]$ . The first of these depends on the inertial mass of energy and the second on its gravitation mass. Exptl. evidence is needed for the existence of both these effects.

F. C. HORT

Magnetism and atomic structure. I. A. E. OXLEY. *Proc. Roy. Soc.* 98A, 264-74 (1920).—This paper is a continuation of previous memoirs on "the influence of mol. constitution and temp. on magnetic susceptibility." (Cf. *C. A.* 14, 3567.) O. points out that it depends on whether radiation problems or unexcited matter is considered as to what interpretation of at. structure must be accepted. He has shown in Part II (*C. A.* 8, 3265) and Part III (*C. A.* 9, 1426) that diamagnetic mols. are complex diamagnets, formed of at least 2 locally magnetic components, which are the rotating electrons with equiv. magnetic moments  $M = eS/r$ , where  $e$  is the electronic charge,  $S/r$  the aerial velocity with which the orbit of area  $S$  is described in time  $r$ . Regardless of the dimensions of the crystal the principal cleavage, if the remaining cleavages are insignificant, is equatorial to the magnetic field if the crystal is diamagnetic and axial if it is paramagnetic. O. has recently worked with naphthalene, anthracene, sodium ammonium racemate, tartaric and citric acids. He confirms Tyndall's rules for other cryst. substances, giving the results on naphthalene. The diamagnetic effect and the cohesive force are maxima parallel to the principal cleavage. O. (*C. A.* 9, 1713) attributes this cohesive force to the mutual induction between a pair of electron orbits. Diagrams of paramagnetic coupling and diamagnetic coupling are shown. By observing the positions in the magnetic field of a crystal, except compds. of simple cubic form, it is possible to isolate the fundamental unit of the crystal structure. These positions depend on the planes of cleavage. The views of O. are consistent with the theory of the cubical atom. Diamagnetic substances are internally self-compensated, probably, by symmetrical distribution of the electron orbits. Magnetic moments of paramagnetic mols. are not so balanced. Rigidity of crystals is

due to magnetic coupling. Fusion is caused by weakening the coupling to such an extent that cryst. cohesion would disappear.

L. D. ROBERTS

Application of the Laue diagram to the determination of the structure of calc spar. ERNST SCHMIDT. *Leipsiger Abh.* 36, 65-213(1910); cf. *C. A.* 14, 1799.—The investigation was undertaken with the object of elucidating suitable methods of detg. indices and of applying the Laue diagram to a useful means of detg. structure. The systematic procedure recommended gives results confirmatory of Bragg's structure model when applied to NaCl. The structure deduced for calc. spar permits a satisfactory explanation of the cleavage relationships from Bragg's model.

J. C. S.

Mass spectra of chemical elements. II. F. W. ASTRON. *Phil. Mag.* 40, 628-43 (1920).—A continuation of A.'s work (*C. A.* 14, 3578) by the use of the positive-ray method to examine elements with reference to isotopy. Seven additional elements have been examd., of which F, P, S, and As are apparently simple elements. B consists of at least two isotopes of at. masses 10 and 11, resp., and although the relative intensities do not satisfactorily explain the observed at. wt. 10.8, present evidence is against the existence of a third isotope, of mass 12. Si is a mixt. of isotopes, of which 28 predominates, 29 appears to exist, and evidence of a more or less positive character indicates the possibility of 30. Br is a mixt. of two isotopes in almost equal proportions of masses 79 and 81, and in all probability there is no isotope of mass 80. In the case of compds. of F and B with Si evidence is obtained for the first time of double charges being carried by mols. instead of atoms. The empirical rule established by J. J. Thomson, therefore, does not appear to be abs.  $\text{BF}_3$  appears to be doubly charged as well as  $\text{BF}_2$  or  $\text{SiF}$  and possibly  $\text{SiF}_2$ . A table is presented showing the results of the isotopic examn. of 18 elements to date, which concludes the list of elements that can be easily introduced into the app. in gaseous form. Certain hitherto unexplained lines are also discussed.

S. C. LIND

The design of soft thermionic valves. G. STRAD. *Phil. Mag.* 41, 470-83(1921).—An exptl. study has been made of the design of satisfactory soft valves for naval use. Two kinds of expts. were carried out: (1) to det. the effect of altering the distance between the grid and the filament, (2) to det. the effect of changing the grid wire spacing. The position of the grid was changed by placing it on a float controlled by Hg so that it could be lowered or raised between the disk and filament. The effect of changing the distance between grid and filament from 3 to 10 mm. was to lower the ratio of grid current to anode current from 3.42 to 0.89. Expts. were made also with a grid of variable spacing between the spiral windings. In a valve with the diameter of the grid helix 6 mm., diameter of grid wire 0.5 mm., the grid spacing giving maximum anode current increases from 2.3 to 2.85 mm. as the grid potential increases from 1.6 to 15 v. Expts. were made also by varying the gaseous atm. Hg vapor, residual air, and argon were used. One of the chief difficulties is to maintain const. gas pressure during operation. Cylindrical construction is most favorable. Soft valves were investigated as oscillators. A method of estimating the gas pressure was worked out by measuring the width of the Crookes dark space in N, A, He, H and CO. The method has the advantage over a McLeod gage of introducing no Hg vapor. After a valve is sealed off from the pump the dark-space method is no longer available, and a new method was invented consisting in measuring the "backlash" current produced by putting a small negative potential on the grid to attract the positive ions produced by shock. The anode voltage necessary to produce a definite current increases as the pressure diminishes. Certain objections to a N atm. were observed and the disappearance of N was studied under different conditions, showing that the action is an electrochem. one. No "clean up" takes place unless the potential between the anode and the negative end of the filament exceeds the ionization potential of N (about 17.5 v.).

S. C. LIND

**The determination of charges on fog particles. A note on E. Radel's article.** REINHOLD FÜRTH. *Z. Physik* 3, 422-4(1920).—F. criticizes Radel (cf. C. A. 15, 464) for using Weiss' formula for the mobility (*Wien. Ber.* 120, 1621(1920)) of small particles from their Brownian movement instead of that of Schrödinger (C. A. 10, 299). R.'s error may be as large as 30%, since he uses only 10 observations of the motion.

F. C. HOYT

**The distribution of the active deposits of radium, thorium, and actinium electric fields.** G. H. BRIGGS. Univ. Sydney. *Phil. Mag.* 41, 357-77(1921).—The expts. were undertaken to decide whether all or only a limiting fraction of the recoil atoms are positively charged at the end of their paths. Two forms of discharge chambers were used, one tubular and the other with circular horizontal plate electrodes. High increase of voltage was found unnecessary as the limiting value was reached with 60v./cm. The fraction of Ra A atoms positively charged was found to be 89.6%. The high values of Henderson (C. A. 9, 2735) are attributed to brush discharge from the edges of the plate and from the cotton fibers used to prevent diffusion. The general conclusion is reached that in all cases a limiting value is attained of less than 100% of induced activity on the negative electrode. This is due to neutralization of the positive charge in part, an explanation different from Ratner's (C. A. 13, 282) elec. wind. The neutralization is much greater in some gases than in others and a connection between the proportion of positively charged recoil atoms and the temp. at which the gaseous medium begins appreciably to dissociate is pointed out in support of the neutralization theory.

S. C. LIND

**Spectroscopic confirmation of the isotopy of chlorine.** A. KRATZER. Göttingen. *Z. Physik* 3, 460-5(1920).—The effect of change of nuclear mass on the series term of the Bohr atom is too small to be exptly. observed. ( $\Delta\lambda = 10^{-6}\lambda^1$  for Cl). For a pure rotation spectrum the effect would be larger, but appropriate data are lacking for a test. For a spectrum due to vibration of 2 masses relative to each other the quantized energy would have to be  $(nh/2\pi)\sqrt{k/M}$ , where  $k$  is a const. depending only on the elec. attraction and  $M$  is the resultant mass  $(1/m_1) + (1/m_2)$ . For HCl, if H remains unchanged while the Cl atom has at. wt. 35 or 37 it follows at once that for the difference of the resulting lines one has  $\Delta\nu = 0.77 \cdot 10^{-4}\nu$ . This is completely confirmed by the series of doublets in the band spectrum of HCl observed by Innes (C. A. 14, 3366). The agreement is quant. within the limit of error, which is about 6%.

F. C. HOYT

**Radiochemistry, the chemistry of the minutest quantities.** O. HAHN. *Pharm. Monatshefte* 1, 180-1(1920).—An address calcd. to present in brief form insight into the character of radioactive and radiochem. investigations.

W. O. E.

**Problems of temperature radiation of gases. (Paper C).** MEGH NAD SAHA. Univ. Coll. Sci., Calcutta. *Phil. Mag.* 41, 267-79(1921); cf. C. A. 15, 468.—The reality of temp. radiation from gases has long been questioned. While some of the permanent gases like H, He, Na, A, N and O remain non-luminous at the highest temps. that can be produced in the lab., the vapors of I, Br, S, etc., become luminous at moderate temps. S. discusses the question of luminous radiation from the stand-point of radiation potential and the quantum theory. The greater the ionization or radiation potential the greater the difficulty of exciting the line spectrum. The resonance or radiation potential of an element is represented by:  $V = (h/e)[(1s) - (2p)]$  in which the notations are the usual ones of spectroscopy and the quantum theory. The lines of the series,  $(1,s) - (2,p)$  are the ones most easily excited to radiation. The presence of a gas with lower radiation potential tends to quench the stimulation of one with higher. This explains the difficulty of exciting the gases with high radiation

potential by temps. available in the lab. The lines are grouped as those due (1) to the normal atom, (2) to the atom which has lost one (the outermost) electron, (3) to an atom having lost 2 electrons, with which a new series of vibrations may begin with the new outermost electron. After discussing the electro- and thermodynamics of line emission under temp. stimulus, S. presents a table for H, He, Mg, and (Ca, Sr, Ba) giving the temps. of complete ionization, of its initiation, and of max. luminescence. For H they are in the order of mention: 24,000° K., 5,000° K. and 12,000° K.; for He 32,000°, 11,000° and 17,000°; for Mg 24,000°, 7,500° and 11,000°; for (Ca, Sr, Ba) 10,000° to 8,000°, 1,500° and 4,000° K., resp. Absorption phenomena and reversal of lines are discussed and explained in terms of the general theory proposed.

S. C. LIND

**Depolarization by light.** EMIL BAUR. Polytech., Zürich. *Z. Elektrochem.* 27, 72-7(1921).—The action of light on polarized Pt electrodes in solns. of  $\text{UO}_2\text{SO}_4$ , eosin, and quinine sulfate has been studied by subjecting the polarization cells to the radiation from a 3000 c. p. elec. lamp. In all cases the current is increased by the light. The depolarization by light is but slightly dependent on the voltage applied, and it is increased by stirring the electrolyte. The results of the investigation indicate that depolarization by light may have its origin in a  $\text{H}_2\text{O}$  photolysis of the illuminated substance.

H. JERMAIN CREIGHTON

**A new effect of radiation.** V. FRITZ WEIGERT. Leipzig. *Z. Physik* 3, 437-59 (1920); cf. *C. A.* 12, 1727; 13, 1185; 14, 1931, 3595.—W. continues his investigations on the effect of linearly polarized light on the absorption of  $\text{AgCl}$ -gelatin films. Direct ultramicroscopic observation shows that the absorption shift and dichromatism are not connected with the complexes of ultramicroscopic size. The disappearance of these effects in the emulsions on changing the Ag into the ionized state shows that during the illumination the amt. of Ag per unit area remains the same, and that the effect is purely physical. W. advances the hypothesis that the effects are due to changes in the "optical packing density" of small, stable Ag complexes of less than ultramicroscopic size. This change is a real or apparent dilation under the influence of the elec. field in the light wave, and has an influence on the absorption of the mol. because the elec. field of neighboring mols. is lessened (in the sense of the Stark effect). The change with density of the absorption of colloidal metallic particles has been investigated quantitatively by Maxwell-Garnett (*Trans. Roy. Soc. London (A)* 203, 389(1904)), and by assuming a form of distribution of the density inside the particles, density-absorption isochromates like those observed can be qualitatively obtained. This requires a decreasing density from the center out.

F. C. HOYT

**Radiology applied to the testing of materials.** A. P. M. FLEMING AND J. R. CLARKE. *Engineering* 110, 850-2, 877-9(1920).—The various types of rays are described as well as the best methods for the production and use of X-rays which can be suitably applied to the testing for homogeneity of materials which are not too thick. A detailed account is given of the app. required for different types of testing. F. O. A.

**X-Ray spectroscopic investigations on cellulose.** II. R. O. HERZOG, WILLI JANCKE AND M. POLANYI. *Z. Physik* 3, 343-8(1920); cf. *C. A.* 15, 983.—A brief geometrical discussion of the interference diagrams obtained with a beam of monochromatic X-rays. A single stationary crystal gives nothing, a crystal powder gives rings, and a bundle of parallel cellulose fibers gives a set of points. Some photographs of this last are shown.

F. C. HOYT

**The intensity of reflection of X-rays by rock salt.** W. LAWRENCE BRAGG, R. W. JAMES AND C. G. BOSANQUET. Univ. Manchester. *Phil. Mag.* 41, 309-38(1921).—The abs. values of the reflecting power of different faces of rock salt have been measured by the ionization method with a Coolidge tube as source of X-rays. The

reflecting power was detd. for 18 glancing angles from  $5.5$  to  $30^\circ$ . The values obtained were compared with the ones calcd. from the theoretical formulas of Darwin and Compton based on the amt. of radiation scattered by a free electron when set into oscillation by rays of given intensity. A strong confirmation of the accuracy of the formulas was obtained, so far as conclusions can be made from the study of one crystal in regard to the arrangement of electrons in the atom. The formula for the amplitude of the wave scattered by each electron holds good for small glancing angles. The values for the effect of the electrons in the Cl atom (FCl) and in the Na atom (FNa) appear to have maxima at about 18 and 10, resp. A uniform distribution of the diffracting points throughout a sphere cannot explain the form of the curve of F as a function of the angle  $\theta$ . The general form of the curve makes it probable that as  $\theta$  increases, the outer electrons for some reason becomes less and less effective in diffracting the X-rays. The result of assuming that they are in vibration is to cause the theoretical curve for F to fall rapidly at first, and then very slowly with increasing  $\theta$ . It seems necessary to make some such assumption to obtain correspondence between the theoretical and observed curves.

S. C. LAND

The absorption of X-rays by chemical elements of high atomic numbers. WILLIAM DUANE, HUGO FRICKE and WILHELM STENSTRÖM. *Proc. Nat. Acad. Sci.* 6, 607-12(1920); cf. *C. A.* 14, 1259.—The authors measure by the ionization method the K absorption limits for the elements from W (74) to U (92).

F. C. HOYT

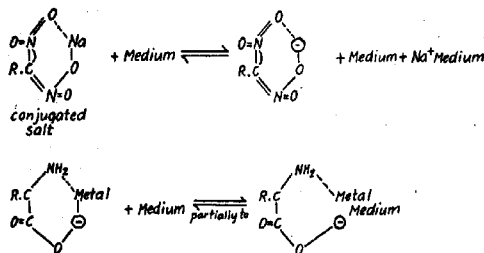
The K-Series of X-rays. WILLIAM DUANE and WILHELM STENSTRÖM. *Proc. Nat. Acad. Sci.* 6, 477-86(1920).—The K-Series emission lines and absorption limits of W are measured by the ionization method.

F. C. HOYT

Absorption of X-rays of long wave length. Connection between X-rays and light. M. HOLWECK. *Compt. rend.* 172, 439-42(1921).—In a preceding note (*C. A.* 15, 338) an app. for the production of long Röntgen waves was described and their absorption in gases was measured. For wave lengths between 100 and  $41 \times 10^{-8}$  cm. ( $\lambda_{\text{min.}}$  of rays produced by 123 to 300 v.) the law of variation of  $\mu/\rho$  as a function of  $\lambda$  is found to be as follows:  $\mu/\rho = 1.0 \lambda^{2.5}$  for O,  $0.8 \lambda^{2.5}$  for N and  $0.2 \lambda^{2.5}$  for H. Comparison with the results of Owen (*C. A.* 12, 2162) shows that the ratio of absorption coeffs. and the laws of variation with  $\lambda$  are sensibly the same for ordinary X-rays and for waves 100 times greater. The absorption coeffs. for soft X-rays are about 105 times greater than for ordinary X-rays. The present note describes app. of higher sensitivity designed to det. what is the least difference of potential between anode and cathode which will produce soft X-rays, and to measure the absorption of these in thin layers of celluloid. Radiation was detected for a p. d. of 25 v. between anode and cathode corresponding to  $\lambda_{\text{min.}} = 493 \times 10^{-8}$  cm. For  $\lambda$  from 40 to  $80 \times 10^{-8}$  cm. the absorption coeff. of celluloid varies with wave length following a  $\lambda^{2.5}$  law similar to that found for gas, but for  $\lambda > 80 \times 10^{-8}$  cm. the coeff. increases more and more rapidly, passing through a max. for  $\lambda = 320 \times 10^{-8}$  cm. and diminishing as the ultraviolet is approached. The radiation from the anti-cathode is too feeble for absorption measurements when the potential between anode and cathode is less than 30 v. For measure of absorption coeffs. these longer waves are obtained with sufficient intensity from ultraviolet light accompanying the ionization of a gas, the wave length minimum being known for the ionization potential. For the wave length corresponding to ionization of H (about  $980 \times 10^{-8}$  cm., Schumann ultraviolet) a layer of celluloid  $2.5 \times 10^{-3}$  cm. thick is found to transmit 20% of the incident radiation, while it allows only 3% of the radiation corresponding to max. absorption ( $\lambda = 320 \times 10^{-8}$  cm.) to pass. This study of absorption for radiations of wave length between 1000 and  $10 \times 10^{-8}$  cm. connects ordinary light with X-rays and reveals the max. absorption existing in this region.

W. F. MROGERS

The function of chromophore. VII. The optical properties of several heavy-metal complexes. J. L. LIFSCHITZ AND ERNST ROSENBOHM. Univ. Zürich. *Z. physik. Chem.* 97, 1-14(1921); cf. *C. A.* 14, 1782.—A study of the spectra of several of the Werner complexes of trivalent Pt, Ir and Rh has shown that these are wholly analogous to the spectra given by similar compds. with the base metals Cr, Mn, Co, Fe, Ni and Sb as central atoms. Since the spectra of all complexes of trivalent metals so far investigated consist of broad, flat, faded bands similar to those produced by colored organic compds., it is assumed that the bands of both classes of compds. result from the merging together of series of single sharp bands. In order to det. regularities in the distribution of the absorptive frequency of such bands, these "series-bands" must first be resolved. Attempts made to resolve the bands of triacetylacetonate complexes of trivalent Co, Cr and Fe in the gaseous condition have been unsuccessful, even though under similar conditions the ultraviolet band of  $\text{OsO}_4$  vapor and the band of *p*-quinone have been resolved. On the other hand, it has not been possible to resolve the bands of  $\text{Ni}(\text{CO})_4$  or those of phoron. For the spectra of the vapor of  $\text{OsO}_4$  and *p*-quinone it has been observed that the bands are arranged in series of the form  $\nu = \nu_0 + na + mb$ , where  $\nu_0$ ,  $a$  and  $b$  are consts. and  $m$  and  $n$  are whole numbers. In the simplest case ( $m = 0$ ) there occurs a series of equidistant bands. VIII. The chromophores of "conjugated" compounds. J. L. LIFSCHITZ. *Ibid* 15-21.—A criticism of Ley's discussion (*C. A.* 14, 2585) of the constitution of the so-called "conjugated" compds. and the bathochromic effect in phenolates. It is pointed out that, in accordance with



the position of the bands, batho- or hypsochromic effects can be ascribed to a definite substitution. As a result of salt formation, a bathochromic effect is not always observed; occasionally no effect at all is produced, and occasionally a hypsochromic effect results when salts are formed from organic acids. A bathochromic effect is not a necessary result of salt formation, and is unnecessary to explain the optical properties of conjugated salts. The independence of absorption of the degree of dissociation, in the case of conjugated salts, is discussed, and the following schemes are given for the dissociation of one of these salts and an inner-complex salt of a heavy metal. In conclusion the structure of the carboxylic acids is considered briefly. H. J. CREIGHTON

The Stark-Doppler effect of canal rays and Stark's resolution of spectral lines in an electric field. K. STURMIG. *Schweiz. Chem. Ztg.* 1920, 392-6.—A brief and simple description of luminous phenomena in glass tubes containing rarefied gas followed by a condensed statement of the 2 most important discoveries credited to J. Stark, the youngest Nobel prize winner in physics. These discoveries are: (1) The Doppler displacement of spectral lines observed in the direction of motion of canal rays, and (2) the sepn. of spectral lines into numerous components when the luminous source is placed in an intense elec. field (analogous to the Zeeman effect of spectral line sepn. in a magnetic field, but of higher order of magnitude). These discoveries have

added much to our knowledge of the elec. processes in gases and assist in attacking the problem of the at. and mol. structure of matter. W. F. MEGGERS.

**Methods of observing the effect of an electric field on spectral lines.** F. TUCZEK AND W. HUCK. *Ann. Physik* 63, 766-72(1920).—All investigations of the Stark effect have heretofore been made with d. c. for operating the discharge tube and direct potential for producing the elec. field which resolves the spectral lines. This applies to both the canal ray method and the method of the first cathode space. In the former method 2 sep. high-potential sources have always been used for tube operation and field production. The great expense of dynamos or batteries for high potential have restricted work on the Stark effect to a few institutions and this investigation was undertaken, therefore, to det.: (1) if a single direct-current generator would not suffice in the canal ray method, and (2) if both methods do not permit the use of a. c. and a transformer. The exptl. results are as follows: (1) In the canal ray method a single d. c. source can be used if the auxiliary electrode is connected with the anode. (2) Both methods permit the use of a current source of variable potential and a transformer. (3) It is advantageous to insert a valve tube in the circuit. W. F. MEGGERS.

**Absorption spectra of organic compounds.** J. J. DOBBIE, E. E. C. BALY AND A. W. STEWART. *Rept. Brit. Assoc. Advancement of Science* 1921, 222-47.—Various theories advanced to explain the absorption bands exhibited by org. compds. are discussed in this report and the position that has been reached in this branch of scientific investigation is stated. Hartley's pioneer work is briefly reviewed, and a very brief account is given of various attempts to coördinate chem. constitution and the absorption of light. Later expts. led to the deduction that the origin of the absorption bands is to be found not in any sp. structure but in a tautomeric equil., that is, in a change or oscillation of linkage. Another important theory is that known as the quinonoid theory which connected visible color with a structure analogous to that of either *p*- or *o*-benzoquinone. This theory is open to serious objection because certain compds., *e. g.*, camphor, in which no oscillation seems possible, exhibit strong selective absorption. The direct structure-absorption correlation theory developed by Hantzsch does not involve any labile atoms but attributes selective absorption to secondary valencies. This also is open to objections. There are 2 general objections to any of the theories that have been referred to. In the first place, no theory can be sound which is limited to a very minute section of the spectrum such as the visible and ultraviolet, and in the second place, no theory can hold good unless it rests on a quant. physical basis. There is also another aspect of the phenomenon of absorption, namely, its undoubted connection with the phenomena of fluorescence and phosphorescence. Just as the selective absorption of light must be due to sp. properties of mols., so also must the emission of light by mols. be due to similar properties. It is evident that any theory must take cognizance of both phenomena. It is true that many theories were advanced to explain the fluorescence of org. compds., but none of these can be said to hold the field. Devised to explain visible fluorescence, they fail entirely to offer any explanation of the ultra-violet fluorescence shown by many compds. A summary of exptl. facts concerning absorption bands and their quant. relationships on the basis of the quantum theory of Planck led to the statement that in formulating a theory of absorption spectra the following relationships which have been established must be considered. (1) Every elementary atom possesses one or more frequencies which are characteristic of the element. (2) When atoms of different elements enter into combination the resulting mol. is endowed with a new frequency which is the least common multiple of the frequencies of the atoms it contains. This is called the true mol. frequency. (3) The central frequencies of all absorption bands, that is, those frequencies for which the absorptive power is greatest, are mol. frequencies characteristic of the

mols., since these alone persist when the substance is cooled to low temps. (4) The mol. frequencies in the visible and ultra-violet regions are exact multiples of a mol. frequency in the short-wave infra-red, which is called the infra-red fundamental frequency. (5) The infra-red fundamental frequency either is the true mol. frequency or is an exact multiple of the true mol. frequency. (6) The breadth of an absorption band as observed at ordinary temps. is due to the combination of the mol. central frequency with subsidiary frequencies. An explanation of absorption is developed on the basis of the quantum theory on which it is assumed that in any elementary atom it is possible to shift an electron from one stationary orbit to another, that a definite amt. of energy is required to effect the change, and that this fixed quantity of energy is connected with the characteristic at. frequencies which are the fundamental constns. from which the whole system of frequencies shown by a mol. is derived. This elementary quantum of energy involved in the electron shift underlies all absorption and radiation. Making the simple assumption that the combining atoms share equally in the energy loss on combination and in the future energy changes of the resulting mol., leads to the conception of mol. quanta, and hence mol. frequency, the latter being the least common multiple of the at. frequencies. The origin of chem. reaction is placed in the electro-magnetic force fields of atoms and the energy changes in formation of mols. can be deduced from the mol. frequencies. Different mol. phases, of which the mol. reactivity will be a function, are shown to exist, depending on the condition of at. and mol. force fields. This mol. phase theory leads to important deductions as regards the energy changes involved in chem. reaction, has an important bearing on catalysis and from the point of view of absorption spectra it leads to the conclusion that a mol. must exist in one of a number of possible phases, each of which is characterized by its own absorption band in the visible or ultra-violet region of the spectrum. It has been proved that a mol. can be brought from one phase to another by the gain of a whole number of fundamental infra-red quanta and this can be brought about by exposure to radiant energy at a frequency characteristic of the mol. Reference is made to the fact that it is possible to change the phase in which a mol. exists by the use of a suitable solvent. In conclusion, it is claimed that this application of the theory of mol. phases to absorption spectra attempts to coördinate on a definite physical basis all absorption spectra observations over the whole spectrum between the extreme limits of wave length  $1000\mu$  and  $0.1\mu$ , and that these attempts seem to meet with considerable success. An appendix gives references to a list of substances of which the absorption spectra have been examd. in the ultraviolet and visible regions since the publication of the last report in 1916.

W. F. MEGGERS

Study of the absorption spectra of potassium ferro- and ferricyanides. F. H. GYTMAN. *J. Phys. Chem.* 25, 147-59 (1921).—In view of the conflicting opinions as to the existence of isomeric ferrocyanides and because of the relatively small amt. of well established data pertaining to the isomeric ferricyanides, this study of the ultra-violet absorption spectra of these substances was undertaken in the hope that new light might be shed on their constitution. A quartz spectrograph was used for making spectrograms and a condensed spark between electrodes of ferro-vanadium and chromium was employed as a source of ultra-violet light. The solns. were examd. in a tube fitted with quartz ends; each exposure was for 10 secs. The careful prepn. of materials, K  $\alpha$ -ferrocyanide ( $K_4Fe(CN)_6 \cdot 3H_2O$ ), K  $\beta$ -ferrocyanide ( $K_4Fe(CN)_6 \cdot 3H_2O$ ), K  $\alpha$ -ferricyanide ( $K_3Fe(CN)_6$ )C and K  $\beta$ -ferricyanide ( $K_3Fe(CN)_6 \cdot H_2O$ ) is described. The exptl. results are given in tables and curves and are summarized as follows: (1) The absorption spectra of the  $\alpha$ - and  $\beta$ -ferrocyanides of K are identical. This fact is taken as evidence that these salts are not isomeric. (2) A slight but well defined difference between the absorption spectra of the  $\alpha$ - and  $\beta$ -ferricyanides of K is established, thus



confirming these salts as isomers. (3) A marked difference is shown to exist between the absorption spectra of the ferro- and ferricyanides of K. (4) On the assumption that the presence of an absorption band indicates a condition of potential tautomerism within the mol., the structural formulas proposed for the ferro- and ferricyanides of K are modified to offer an opportunity for tautomeric chance, thus giving a possible explanation of the presence of bands in their absorption spectra. (5) Furthermore, it is pointed out that the relative number and position of the tautomeric groups within the mol. may possibly be the cause of the marked difference between the absorption spectra of the ferro- and ferricyanides of K.

W. F. MCGOWAN

A review of the series in the spectra of the elements. F. A. SAUNDERS. *J. Optical Soc. Am.* 5, 1-11(1921).—S. gives a brief review of our present exptl. knowledge of line series, calling attention to the incomplete character of this knowledge, in spite of its great theoretical importance for the problem of at. structure. At present theory has, in many respects, run far ahead of expt., predicting the possibility of numerous series and combination lines not yet detected in the lab. This is especially true in the case of enhanced spectra, due to an ionized atom. The simplest line spectra occur in the case of an atom with one electron in the valency ring (alkali metals), and the complexity mounts as the number of electrons increases, reaching a max. for the noble gases. Our knowledge is in inverse ratio to this complexity.

R. T. BIRGE

The corpuscular spectra of the elements. MAURICE DE BROGLIE. *Compt. rend.* 172, 274-5(1921).—A body, under the influence of X-rays, emits characteristic X-rays and also "photo-electric" electrons of high velocity. These latter have been little studied. By deviating the electrons in a magnetic field, a "magnetic spectrum" can be produced, and it has been shown that two classes of homogeneous rays are present, corresponding by the quantum relationship to the K lines. The author now finds, in studying elements from  $N = 42$  to 56 that there is a continuous "electron emission band," corresponding to the K absorption band, having a sharp edge on the low velocity side.

R. T. BIRGE

Magneto-optic investigations of the nitrogen band 3883. ALBERT BACHERM. *Z. Physik* 3, 372-88(1920).—B. exams. the effect of a magnetic field on this band with a very high dispersion. Forrat's (*Ann. de Physique* 3, 282(1915)) expression for the "simplification,"  $n \, dn/H_2$  ( $n$  = frequency,  $H$  = field strength, is not const. for different lines of a series or for the same line for varying  $H$ . It decreases with increasing series number and increasing  $H$ . The expression  $n \, dn/H_2(n - dn/n)$ , however, remains const. with increasing magnetic field for most doublets and anomalies. For accidental line pairs and for triplets of the  $A$  and  $B$  series there is a small effect of the magnetic field for which no definity law was found. Their magnetic behavior helps to classify some of the doubtful lines and seems to uphold Heurlinger's assumption that the series numbers should begin with the line of smallest intensity and go in both directions with + and — signs.

F. C. HOYT

A uniform development of the Balmer and Deslandres terms. A. SOMMERFELD. *Arkiv. Mat. Astron. Physik.* 15, No. 8(1920).—In this, S.'s first contribution to the theory of band spectra, attention is called to the 2 types of "rotator." In one the moment of inertia ( $J$ ) is practically unchanged by rotation, such as the earth and its flattening. In the other, such as the Bohr H atom, the moment of inertia varies greatly with the position of the encircling electron. Quantelation of the first type, with  $J$  assumed const., leads to the Deslandres term  $Am^4$ , while from the second type is derived the Balmer term  $R/m^4$ , ( $R$  = Rydberg const.), thus connecting theoretically band and line spectra. Attention is called to the work of Lenz (*C. A.* 14, 2296) on the many lined spectra of H, proving that the Bohr model of  $H_2$  cannot be correct. (See S.'s "Atombau und Spectralinien," 2nd ed., pp. 650-52.)

R. T. BIRGE

**Variations in gas pressure caused by electric discharges in spectrum tubes and centers of luminescence.** L. HAMBURGER. *Proc. Acad. Sci. Amsterdam* 23, 279-94 (1920).—Pressure differences as high as 30% of the total pressure may occur in Geissler tubes where the positive and negative chambers are separated by a capillary. This pressure is caused by actual mass transference of ions by the current and is much greater than a pressure due to the electric wind. The extent of the pressure difference varies with the number, mass, charge and mobility of the positive and negative ions. It depends, therefore, on the elec. variables, the gas pressure and the nature of the gas. Some calcs. are made as to the possible effects of changing some of these factors and the results compared with the exptl. data. A discussion is given reviewing the close connection of optical, chem. and catalytic properties inherent in the outer electrons of the atoms.

F. O. ANDEREGG

**Theory of the shift toward the red of lines in the solar spectrum.** M. v. LAUE. Berlin. *Z. Physik* 3, 389-95(1920).—A proof of the following is strictly necessary for the validity of Einstein's reasoning concerning the shift toward the red of spectral lines: The period of a vibrating mechanism, measured in the "proper time" of the mechanism, has a value characteristic of the mechanism and independent of the metrical tensor  $g_{\mu\nu}$ . From this it follows that periods measured in local time for the same clock at different places are as the potentials  $g_{44}$ . L. proves this law for a general oscillatory mechanism, and also shows that it holds from energy considerations if Bohr's frequency rule is true.

F. C. HOVR

**Spectroscopy.** A. FOWLER. *Engineering* 111, 233-4(1921).—Report of a lecture dealing with the regularities which have been found in spectra and the light thus thrown on at. structure and on the nature of radiation. The Balmer, Lyman and Paschen series of H are described and explained on Bohr's theory. The spectra of elements of higher at. wt. than H are similarly represented by sets of series. In general, there are 4 main series known, resp., as the principal, the sharp, the diffuse and the fundamental series.

W. F. MEGGERS

**The oxidation and luminescence of phosphorus.** I. HARRY B. WEISER AND ALLEN GARRISON. *J. Phys. Chem.* 25, 61-81(1920).—The luminescence of P is due to the oxidation of its vapor. If there is a deficiency of O the zone of reaction spreads outward. If there is an excess of O the zone of reaction is driven in toward the solid P, and a coating of oxide is formed on the surface. This hinders further vaporization of the P and stops the reaction. Extinction of the luminescence in pure O is thus explained at last. The "extinction pressure" of the O is a function of the temp. because the extinction depends on the vapor pressure of the P. Conflicting observations of earlier workers and the comprehensive expts. of Weiser are all in accord with this theory. The combined influence of temp. and the partial pressure of O on the rate of evapn. of an oxidizable substance is important in other systems also.

TORRINGTON DANIELS

**Inorganic luminescent phenomena. II. Luminous boron nitride (Balmain's aethogen and the flame excitation of luminescence).** ERICH TIERDE AND F. BUESCHER. Univ. Berlin. *Ber.* 53B, 2206-14(1920).—BN was prepd. by 4 methods: (1) by Balmain's method (*Phil. Mag.* 1842, 422; 1843, 467) where boric acid was mixed with metal or better cyanide and heated to 1200° for 30 min.; (2) 1 part of boric acid was heated with 2.5 parts urea in a gas furnace; (3) borax and  $\text{NH}_4\text{Cl}$ ; (4) thermal decompn. of the addition compd. of  $\text{BCl}_3 + \text{NH}_3$ , which gives a very pure nitride. The conditions of prepn. were varied widely. On exciting with the luminous mantel of the Bunsen flame, preps. (1) gave a whitish green color, while some of (2) and all of (3) gave a bluish light. Preps. (4) and the rest of (2) were not excited by a flame. Flames of H,  $\text{H}_2\text{S}$ , CS, EtOH, etc., and especially Cl burning in excess H gave good effects.

Those preps. which were excited by a flame were also caused to phosphoresce under the action of day-, arc- and Hg-vapor light, as well as when bombarded by X-, cathode- or Ra-rays. The non-luminescent preps. were practically pure, and it was found that from 5 to 10% boric acid was required for flame luminescence. On melting inactive material with boric acid under the blow pipe it became active. With more than 10% boric acid a new class of phosphorescence set in of a sky or cyanogen blue color, which persisted for some time. It was not detd. whether there were present traces of metals or of other nitrides which might possibly have a hand in the luminescence. The work of Donau (*C. A.* 7, 3445; 10, 3025) and Paneth (*C. A.* 13, 1431) on the action of traces of Bi or Mn compds. in promoting luminescence of  $\text{Ca(OH)}_2$  was repeated and confirmed and the phenomenon was considered analogous to the luminescence of BN. On viewing this luminescent BN through a direct vision spectroscope the flame characteristic of boric acid was obtained, *i. e.*, a continuous spectrum from 670 to  $430\mu$ , which had a region of greatest intensity at  $560\text{--}510\mu$ . The compd. is luminescent even at bright red heat. The luminescent action of the Cl flame burning in H indicates that it is not caused by ultra-violet light; this leaves as a possibility the assumption that the luminescence is due to electrons and other ions just as the green inner cone of the outer Bunsen flame is thought to be aluminescence caused by ions. Finally, careful test of the hypothesis of Ren   (*C. A.* 6, 3040) that the luminescence was due to some kind of X-ray gave negative results. III. Phosphorescence of boric acid. ERICH TIED  . *Ibid* 2214-6.—Orthoboric acid was dried in the dark and tested for a phosphorescent effect as the drying slowly proceeded. At about  $70^\circ$  a notable afterglow was produced which increased rapidly as the water was removed to a max. where the light had a great intensity although short duration. This max. does not correspond to any definite compd. The effect fell off rapidly on drying until pure fused boric acid was not excited by light until a trace of water had been added again. Similar results were obtained by varying the conditions of drying. This phosphorescent effect was produced not only by flames but also by cathode-, X- or Ra-rays. F. O. A.

Phototropy. H. STOBBE. *Chem. Ztg.* 44, 340(1920).—In the course of the last decade the following phototropic substances have become known: quinoquinoline-HCl, tetrachloroketonaphthalene, 66 hydrazones and osazones, 15 anils, 19 fulgides, 24 fulgide derivs., 5 diacylaminostilbenedisulfonic acids and several others. Fulgides and anils retain their phototropic property when dyed on wool, cotton, silk and paper, when mixed with colloids such as collodion and resins and also in undercooled fusions. Mallison has shown that the intensity and wave length of light, the temp. and the nature of the glass vessel surrounding the phototropic substance affect the sensitivity of the substances to phototropic change. The sulfonic acids are not sensitive in an atm. of H, are only weakly sensitive in an atm. of  $\text{CO}_2$ , strongly sensitive in air and very strongly sensitive in pure O. These substances form deeply colored oxygen addition products, which decompose in the darkness. The oxygen is evolved as  $\text{O}_2$ . The salts of sulfonic acid undergo similar changes. The hydrazones and osazones behave entirely differently; they are more sensitive in an atm. of H and of  $\text{CO}_2$  than in air or oxygen, and they do not evolve ozone in the reverse change in the dark. It is concluded that phototropic changes are in part chem. and in part physical. ISMAR GINSBERG

Hering's color mixer for spectra light. S. GARTEN. *Z. Biol.* 72, 89-100(1921).—A description of a modified and improved app. for color mixing in spectrum analysis. F. S. HAMMETT

Certain numerical relations which the atomic weights present (JANDRIER) 2. The velocity of transmigration of ions in crystals (HEVESY) 2. Dissociation of halogen

compounds (WEINBERG) 2. The nature of secondary valence (SMITH) 2. The spectrochemistry of benzene derivatives (AUWERS) 10.

#### 4—ELECTROCHEMISTRY

COLIN G. FINK

**Latest developments of the electrochemical industry (Japan).** YOGORŌ KATO. *J. Chem. Ind. (Japan)* 23, 788-75(1920).—New electrochem. industries developed in Japan since the war are: (1) electrolytic Zn, Pb, Ni, production of NaOH, Cl and bleaching powder, O and H, storage batteries metallic Na, Mg and NaHCO<sub>3</sub>, and other chemicals; (2) carborundum, artificial graphite, ferro-alloys, elec. steel of all kinds, pig iron, HNO<sub>3</sub> and alundum; and (3) Cottrell's process. A brief discussion of electronic phenomena is appended. S. T.

**Electrochemistry and electrometallurgy in the west.** L. W. CHAPMAN. *J. Elec. West. Ind.* 46, 130-1(1921).—The availability of water power and ores is an important factor in the development of electrochemistry and electrometallurgy in the West. The location of a number of important plants is given. D. MACRAE

**Electric furnace for the production of ferromanganese.** E. S. BARDWELL. *J. Elec. West. Ind.* 46, 120-2(1921).—In the elec. furnace, elec. energy supplies the heat necessary to bring the charge to a temp. sufficiently high to bring about reduction. The size and shape of furnaces, the design of electrode holder and the types of electrodes are discussed. The greatest single advance has been the introduction of the Söderberg self-baking electrode. Whether the elec. furnace can compete with the iron blast furnace is very problematical. (Cf. C. A. 14, 1483.) D. MACRAE

**Electric smelting of pig iron at Domnarfvet, Sweden.** GERRARD DE GERR. *Chem. Met. Eng.* 24, 429-33(1921).—A brief history of the development of the Domnarfvet Iron Works and a description of the present equipment and practice in the production of elec. pig-Fe. Originally intended for the production of material of high quality for export, this plant later produced ordinary Fe for domestic consumption. After the invention of the basic steel process, basic Bessemer and open-hearth plants were built to utilize the high-P ore belonging to the company. This caused an increased demand for pig-Fe which the original charcoal blast furnaces could not meet. The latter were accordingly rebuilt for coke. The coke had to be imported, was poor in quality, and the output of pig-Fe was still too low. Hence, in considering further construction, the possibilities of elec. pig-Fe smelting were investigated. Early tests showed that elec. pig-Fe could compete with Swedish charcoal Fe, of high quality but not with ordinary Fe. Consequently, the construction of more coke blast furnaces and coke ovens was decided upon and work actually started. The war then brought the price of coke to a prohibitive figure, the plans were changed, and installation of elec. furnaces and the development of water power was hastened. At present 6 elec. pig-Fe furnaces are built or under construction, 5 Electrometals (of from 3,000 to 5,500 kw. nominal transformer capacities) and 1 Helfenstein (9,000 kw.). The latter was not operating in 1920. Total capacity of the 6 furnaces is 31,000 kw. Assuming an output of 3.6 tons of pig-Fe per kw. yr., the capacity of the Electrometals furnaces is about 80,000 tons per yr. The causes for "hot runs" and "cold runs" (too much C or too little C, respectively) and the remedies are considered. Even with the furnace running normally, there is difficulty in regulating the temp. of the pig-Fe as an increase of amperage increases only the rate of melting and not the temp. of the Fe. The superheat desirable to avoid losses in runners and skulls during tapping and transportation of the Fe is often difficult to obtain. The materials required per ton of pig-Fe produced

are Fe ore 1720 kg., limestone 60 kg., charcoal 370 kg., electrodes 8 kg., and power 2400 kw.-hr. Coke and anthracite have been considered for reducing agents in place of charcoal. A mixture of coke and charcoal, 50% of each, can be used, but with any higher % of coke or with coke alone, the results are poor. Both pit and shaft furnaces for producing elec. pig-Fe have been run at the same time on a large scale at Donnarivert. The tests were decidedly in favor of the shaft furnaces.

LOUIS JORDAN

**Electric furnaces for non-ferrous metals.** J. B. C. KERSHAW. *Engineer (London)*, 131, 48-50(1921); illus.—A review. Some details of design and construction of American brass-melting furnaces (Ajax-Wyatt, Booth, Detroit, Rennerfelt, Snyder) are given. The Wile Sn-smelting furnace (*C. A.* 9, 1581) is also considered. L. J.

**English and American types of electric iron and steel furnaces compared.** J. B. C. KERSHAW. *Foundry Trade J.* 23, 5-7, 29-30(1921); illus.—A review of American elec. steel furnace design and practice for comparison with Campbell's review of English practice (*C. A.* 14, 2752). The Booth-Hall, Girod, Greaves-Etchells, Grünwall-Dixon, and Héroult furnaces are described.

LOUIS JORDAN

**Discussion on "electric steel."** R. J. WEITLANER. *Blast Furnace Steel Plant* 9, 209(1921).—W. takes exception to statements in Carlisle's paper (*C. A.* 15, 227), viz., as to what reaction causes resulfurization of the bath and the statement that the size of the elec. furnace is mainly the cause of higher S and P in the product. W. thinks that the relation of time to tonnage and the vol. of slag to vol. of metal is more important than mere size of the furnace and surface area of the bath in explaining the difference between small and large furnaces in the elimination of S and P. L. J.

**Electric furnaces for making steel (Stassano furnace).** I. ALFRED STANSFIELD. *Blast Furnace Steel Plant* 9, 189-93(1921); illus.—Elec. steel furnaces are classified and the general characteristics and advantages of each type are given; the Stassano furnace is described in detail. Elec. steel furnaces may be classified as arc furnaces and resistance furnaces: (I) Arc furnaces are either (1) independent arc or (2) direct heating arc furnaces; these latter may again be divided into (a) series arc and (b) electrode-hearth furnaces. (II) Resistance furnaces are either (1) induction or (2) resistor type. The independent arc furnace can be operated empty and works well on cold scrap, but the transfer of heat to the charge is less perfect than in the direct arc. The direct arc gives high slag temps. desirable in the elimination of S in refining steel. In the series arc furnace, 2 arcs are operated in series (e. g., the Héroult), while in the electrode-hearth type the hearth constitutes one electrode (e. g., the Girod). Most resistance furnaces are of the induction type although some utilize a resistor other than the steel itself in which to generate heat. The two most important examples of independent arc furnaces are the Stassano and the Rennerfelt. The Stassano furnace is heated by a 3-phase arc between 3 nearly horizontal electrodes. This furnace has been built stationary, revolving, tilting, and oscillating. It operates on 75 to 150 v. and has a power factor of 90-95%. The heat of the arc spreads generally throughout the furnace and, as a consequence, the thermal efficiency is not very high and the roof of the furnace needs frequent renewal. Operating data for several installations and a short bibliography for the Stassano furnace are given.

LOUIS JORDAN

**The influence of the electric furnace on the metallurgy of non-ferrous metals.** H. M. ST. JOHN. *Trans. Am. Electrochem. Soc.* 40, preprint(1921).—A detailed survey of the elec. brass industry. The introduction of the elec. furnace has meant the melting of brass high quality and bronze in ton lots, or approximately ten times the amount of the average crucible heat; greater economy in metals; inclusion of Zn and other white metals directly in the charge originally placed in the furnace, thus eliminating the laborious and expensive speltering process; the elimination of O, S and other con-

terminating elements, from the atm. to which the molten metal is exposed; a marked reduction in the overall cost of melting Cu alloys, as compared with fuel-fired furnaces.

C. G. F.

**Electric annealing and heat-treating furnaces.** GEO. P. MULLS. *Assoc. Iron & Steel Elec. Eng.* 3, 1-20; *J. Eng. Club Philadelphia* 38, 25-31(1921).—Temp. control with 2-point and single-point recorder controllers and with the rate of change controller is described. There have been installed or contracted for up to the present time approx. 12,000 kw. capacity in ribbon-resistor type elec. furnaces for temps. of from 550° to 1000°. Some of the typical installations are described as well as an exptl. furnace for treating armor-piercing shells and a lay-out for annealing 120 tons of steel castings per 24 hrs.

LOUIS JORDAN

**Thermal characteristics of electric ovens and hot plates.** W. CRAMP, *et al. Electrician* 86, 357(1921).—Discussion of the paper of Griffith and Schofield (*C. A.* 15, 1105.

C. G. F.

**Metallographic investigation of copper electrolytically deposited in presence of gelatin.** G. GRUBB AND V. RUESS. *Techn. Hochschule, Stuttgart. Z. Elektrochem.* 27, 45-52 (1921).—A study of the electrolytic deposition of Cu from CuSO<sub>4</sub> solns. containing gelatin shows that the deposition proceeds in 2 distinct steps. During the 1st stage a malleable skin is formed, consisting of the disperse system Cu-gelatin, in which the dispersion medium gelatin contains the charged Cu in the dispersed state for some time. The 2nd step consists in the consolidation of the ppt., whereby the Cu is formed into coarse particles, and the Cu and gelatin alternately deposit one over the other in layers. The time elapsing between the two stages has been calcd. from microscopic data. The calcd. results have been confirmed by voltage measurements.

H. JERMAIN CREIGHTON

"The metallographic investigation of electrolytically deposited copper." G. GRUBB. *Z. Elektrochem.* 27, 53-4(1921); Addendum. See preceding abstract.—The results presented in the previous paper are compared with those obtained by Sieverts and Wippelmann (cf. *C. A.* 9, 3173; 10, 854), and the structure of electrolytically deposited Cu is discussed.

H. JERMAIN CREIGHTON

**Electrolysis of cerium salts in aqueous solutions.** A. B. SCHÖTZ. *Tidskrift Kem.* 17, 213-5, 228-32(1920).—In this work the double chlorides with Fe were used as raw material. Lactic acid was used in place of HCl to increase the voltage. As rotating cathode S. used Pb-plated Pt. The anode chamber was a glass tube with a helical row of openings. The anode was a Pt wire wound around the tube through which the liquid of the anode chamber was drained. The cathode was dome-shaped, and inverted over the anode chamber and anode. The products formed consisted of an alloy of Fe and Ce, in which Ce varied from 59.4 to 62.8% (in one exceptional instance 67%). S. is of the opinion that the ppt. as formed contained no oxides but found it difficult to prove this point on account of the strong tendency of the metals to oxidize on drying. There was no gas evolution at the cathode.

A. R. ROSE

**An improved form of battery separator.** T. A. WILLARD. *Electrician* 86, 355 (1921).—The sheets of grooved wood now commonly employed as separators in secondary batteries, though a great advance on the original glass rods, suffer under the disadvantage of having a somewhat limited life, with the result that the maintenance costs are increased to a not inconsiderable item, and the efficiency of the battery is reduced owing to the fact that taking down and setting up are necessary when replacement occurs. The new Willard separator consists of base of the purest Para rubber reinforced with a very large number of thin cotton threads. These threads act as capillaries through which the electrolyte can percolate. Another advantage of the new separator is that heavier discharges of the battery are possible.

C. G. F.

**Routing storage batteries through a repair shop.** H. C. HEIDRICH. *Elec. World* 77, 831-2(1921).—A detailed illus. account of the repair shop methods of a large concern in Newark, N. J. C. G. F.

**Barrel rheostat handles 1,600 amperes at 125 volts.** F. H. BROOME. *Elec. World* 77, 872(1921).—Illustrated account of a simple water-cooled rheostat. Its total cost is about \$150. C. G. F.

**Electrostatic deposition of dust from blast-furnace gas and extraction of potash therefrom.** E. BURY, A. BURY, O. OLLANDER AND F. BAINBRIDGE. *Iron & Coal Trades Rev.* 102, 191-2(1921).—The Cottrell and Lodge methods are compared. An elec. pptn. plant (Lodge) installed at Skinningrove Ironworks proved that with 85-90% of installation operating, the dust in the gases could be reduced from 5-6 g. per cu. m. in the dirty gas to 0.8-1.1 g. in the cleaned gas. The cleaning was effected with comparatively small heat loss; the raw gas enters at 220-250° and the cleaned gas leaves at 200-220°. The installation recovers 40 to 50 tons of dust per week containing 20 to 27% KCl. S. D. KIRKPATRICK

**Electrical precipitation of dust (talc).** E. LEVÊQUE. *Industrie chimique* 8, 15-7 (1921).—Abridged account of a lecture giving a brief historical sketch of the process, outline of the method of obtaining the elec. field required, and a very brief description of the equipment furnished by the Société de Purification Industrielle des Gaz for the pptn. of SO<sub>2</sub> and of talc. A. P.-C.

**Silk-film device prevents damage to opened current transformer.** R. H. N. LOCKYER. *Elec. World* 77, 655(1921).—Two brass spring contacts, connected to the terminals of the secondary of a current transformer, are sepd. by a silk film. This film punctures when an open circuit occurs in the secondary of a current transformer carrying load and the short circuit, thus established, prevents the induction of a dangerous potential and protects the transformer from damage. LOUIS JORDAN

Some electrical causes of dust explosions (PIERCE) 24. Electric testing furnace (ANON.) 19. The liquefaction of carbon (RISHKEVICH) 2. Electrolytic oxidation of methanol and of ethyl alcohol in alkaline solution (MÜLLER, MIRO) 10.

**Primary electric battery.** P. B. HYDE. U. S. 1,369,813, Mar. 1. Structural features.

**Storage battery.** H. MCCREARY. U. S. 1,369,931, Mar. 1. Structural features.

**Storage batteries.** B. FORD. U. S. 1,370,011-2-3, Mar. 1. Structural features.

**Storage battery.** C. D. GALLOWAY. U. S. 1,370,014, Mar. 1. Structural features.

**Storage battery.** E. W. SMITH. U. S. 1,370,058, Mar. 1. Structural features.

**Storage-battery separators.** G. STEERUP. U. S. 1,370,064, Mar. 1. Wood separators are prepd. for use by steaming to open the pores of the wood, impregnating with NH<sub>3</sub>, and then volatilizing the free NH<sub>3</sub> and its compds. from the wood and treating the latter with steam at a temp. of about 125-130° for several hrs.

**Dry battery.** A. W. SCHORGER. U. S. 1,370,052, Mar. 1. In making dry cells, the molded cathode is dipped into a magma of plaster having an admixture of starch and the thin envelope thus formed is allowed to harden on the cathode. The latter is introduced into a Zn electrode and gelatinizable electrolyte containing ZnCl<sub>2</sub> is poured in to act on the starch and disrupt the envelope and give a better contact with the cathode.

**Dry batteries.** W. B. SCHULTZ. U. S. 1,370,054-5, Mar. 1. Structural features.

**Dry battery.** W. B. SCHULTZ. U. S. 1,370,056, Mar. 1. An electrolyte paste for dry batteries is prepd. by adding  $\text{ZnCl}_2$  14.3,  $\text{NH}_4\text{Cl}$  9.1 and  $\text{H}_2\text{O}$  13.6 parts to a mixt. of cereal 24.5,  $\text{ZnCl}_2$  3.8,  $\text{NH}_4\text{Cl}$  10.6 and  $\text{H}_2\text{O}$  24.1 parts. Admixture of the ingredients in this manner produces a gelatinous electrolyte.

**Acid-proofing wood battery containers.** R. N. CHAMBERLAIN. U. S. 1,369,783, Mar. 1. Wood battery containers are immersed in linseed oil to fill the pores of the wood and then given a coating of asphalt paint before the linseed oil is dry, to render the wood acid-proof.

**Continuous production of calcium cyanamide.** A. LANG. Ger. 319,798, Nov. 21, 1917. The carbide is mixed, in a nozzle, with N preheated to the reaction temp., and the mixt. is blown under pressure into the reaction chamber provided for that heating unit. As a result, the reaction mass is more intimately mixed than heretofore, thereby facilitating the action of the N upon the  $\text{CaC}_2$  to be nitrogenized and increasing the yield of the "nitro-lime." Details of construction are specified.

**Arc lamps; vacuum tubes.** BRITISH THOMSON-HOUSTON CO. Brit. 147,815, July 9, 1920. An inert gas in an inclosed arc device having an incandescent cathode is kept pure by a substance which combines with foreign gases such as N, H, and  $\text{H}_2\text{O}$  vapor, evolved by the electrodes and walls of the envelope during use. The resulting compds. have a negligible vapor pressure. Lower elec. pressures are then sufficient.  $\text{P}_2\text{O}_5$  may be employed as the purifying agent when the bulb is filled with N. For the monatomic gases A, Ne, Kr, X and He, Mg, Ca, or a similar metal is suitable, but  $\text{P}_2\text{O}_5$ , it is stated, also appears to combine with H and N to some extent.  $\text{CO}_2$  also may be used for filling the bulb. The gas, which suppresses electrical disintegration of the cathode, may have a pressure varying from several mm. of Hg to about an atm. For a low-voltage rectifier, A at 5–12 cm. of Hg is suitable. In a Ne tube, the pressure may be half an atm. The purifying substance, in the form of wire or strip, may be wrapped around a leading-in wire near the hot cathodes so as to become vaporized; or the substance may be inclosed in a sealed capsule, which is placed in an open tube and broken by shaking after the bulb is sealed. The incandescent cathode may be of material fusing above about  $2000^\circ$ , such as W, Ta, or C. The anode may be of W, C, Hg, or the like. An envelope of Na-Mg borosilicate glass may be used.

**Electrolytic rectifiers, etc.** METROPOLITAN-VICKERS ELECTRICAL CO. Brit. 155,579, Dec. 2, 1920. An electrolyte for use in electrolytic cells such as lightning arresters, condensers, rectifiers, etc., consists of any known film-producing soln. containing a small quantity, usually less than 1%, of a non-film-forming salt such as Na or K nitrate or sulfate, or a halide such as Na fluoride, fluosilicate, fluoborate, fluotitanate or fluoarsenate. A small quantity of free alkali may also be added. In one example the electrolyte consists of 30 g. boric acid, 5 g.  $\text{NH}_4$  borate, 4 g. NaOH and  $\frac{1}{2}$  g.  $\text{Na}_2\text{F}_2$ , all dissolved in 1 l. of  $\text{H}_2\text{O}$ . In another example, 2–10 g. NaOH are used and  $\frac{1}{2}$ –3 g.  $\text{Na}_2\text{F}_2$  with the above quantities of boric acid and  $\text{NH}_4$  borate. The electrodes consist of Al, Mg, Ti or other film-forming metals. The films on the electrodes may be formed in the electrolyte or in a sep. electrolyte of ordinary constitution.

**Apparatus for electrolyzing water.** I. MARSUSE. Japan 36,327, May 5, 1920. The app. is made of a V-form sectional vessel with a perforated electrode of the same form.

**Apparatus for electrolyzing metal salt solutions.** FREDERIKSTAD ELEKTROKEMISKE FABRIKKER AKTIESELSKAB. Norw. 30,995, Aug. 16, 1920. Anode and cathode chamber are sepd. by a layer of loose granular material which rests, evenly distributed, upon and over a bottom permeable to the liquid. The bottom is inclined to such a de-



gree that the granular material charged in from above is distributed uniformly, by its own wt., over the entire surface of the bottom. Cf. C. A. 14, 1788.

**Zinc plating.** Z. SUGAWARA. Japan 36,192, Apr. 15, 1920. The electrolyte is prepd. by dissolving  $\text{ZnSO}_4$ , alum and  $\text{NH}_4\text{Cl}$  in  $\text{H}_2\text{O}$ . An Al anode is used. An e. m. f. of 10-20 v. is applied.

**Treatment of tungsten and allied difficultly fusible metals.** C. YOKOTA and DAI-NIPPON ELEC. LAMP CO., Japan 36,028, March 22, 1920.  $\text{WO}_3$  and other oxides are heated electrically with addition of Si, B, Al, or P, etc., in reducing gases like  $\text{NH}_3$  or  $\text{H}_2$  to a fused state and are then cast; pure metals are obtained.

**Electrical treatment of high-melting metals, their compounds or mixtures.** E. AOYAGI. Japan 36,000, March 18, 1920. Rods of W, Mo, Ta, rare earth metals, alk. earth metals, their compds. or mixt. are heated electrically in a vertical position in an atm. of neutral or reducing gases to near their m. p. and then extended to proper length, giving them annealed properties suitable for elec. filaments.

**Melting brass.** W. R. CLARK. U. S. 1,370,090, Mar. 1. Brass or similar scrap in the form of loose chips or cuttings is formed into cabbages and the latter are slowly moved toward an elec. furnace and thereby preheated and then are introduced into the furnace.

**Electric hearth furnace adapted for melting metals.** H. A. GREAVES and H. FETCHELLS. U. S. 1,370,018, Mar. 1. The furnace operates on 3-phase a. c.

## 6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

**The reaction between nitric acid and copper.** L. S. BAGSTER. Univ. Queensland. *J. Chem. Soc.* 119, 82-7(1921).—B. works on the theory that in the equil. between  $\text{HNO}_3$ , NO and  $\text{HNO}_2$  the  $\text{HNO}_2$  reacts with a H film formed on the surface of the Cu, thus taking the Cu into soln. and itself being reduced to hyponitrous acid. A secondary reaction takes place between the hyponitrous acid and the  $\text{HNO}_3$  to give  $\text{HNO}_2$ . Exptl. data (using 0.250 g. of Cu and 10 times the required amt. of acid) show that for  $\text{HNO}_3$  from 5 to 14.5 N almost a theoretical quantity of  $\text{N}_2\text{O}_3$  is given off, the excess N giving  $\text{N}_2\text{O}_4$  varying in % from 80 for 14.5 N to approx. 9.0 for 5 N. S. A. BRADLEY

**Which elements form gaseous hydrides?** FRITZ PANETH. *Ber.* 53B, 1710-7 (1920); cf. C. A. 14, 3374.—In addition to the elements standing in the periodic system 1-4 places before a noble gas should be included B, which stands 5 places before Ne. Its valence is 4 in the hydrides thus far accurately investigated by Stock. A. R. M.

**Chromic thiocyanates.** NIELS BJERRUM. *Det. K. Danske. Vidensk. Selskabs Skrifter, Nat. Math.* 7, 66(1915).—A full account is given of the complex chromic thiocyanates and their equil. Tervalent Cr yields the following complex ions with  $\text{H}_2\text{O}$  and CNS ( $\text{CNS} = \text{X}$ ), in which the water is replaced step by step by the CNS radical:  $\text{Cr aq}^{+++}$ ,  $\text{Cr aqX}^{++}$ ,  $\text{Cr aqX}_2^+$ ,  $\text{Cr aqX}_3$ ,  $\text{Cr aqX}_4^-$ ,  $\text{Cr aqX}_5^{--}$ , and  $\text{CrX}_6^{---}$ .  $\text{Cr aqX}_3$  is a nonelectrolyte. The existence of the second and third complexes could be established in soln., but the corresponding substances could not be isolated in the solid state; they are insol. in ether. *Trithiocyanotriquoichromium* could be obtained in the cryst. condition, but not in a state of purity; in soln. it can be prepd. in a much purer form. The mol. cond. of a 0.1 N soln. of the crystals is  $\mu = 3.87$  at  $0^\circ$ , while under similar conditions, the value  $\mu = 250-300$  is in general observed for a trivalent electrolyte. When dried in a vacuum, the very hygroscopic crystals retain 3.2-3.6  $\text{H}_2\text{O}$ , which is obviously chemically combined in the complex. The *tetrathiocyano* complex could be obtained in the form of a dil. soln. of the free acid, from which the corresponding

salts were prepd., but could not be isolated in the solid state. Quinine and strychnine yielded ppts. of varying compn.; quinoline salts gave an oily ppt. The free acid is freely sol. in ether, in which the salts do not dissolve. The *pentathiocyno* complex was isolated as the beautifully cryst. *quinoline* salt, from which the free acid and the *sodium* salt were prepd. It contains 1 H<sub>2</sub>O in complex union; the free acid is sol. in ether, but the salts are not. The *quinoline* salt (which does not contain water of constitution), and the *pyridine* salt of the hexathiocyno complex are described. All the chromothiocyno complexes give reddish violet solns. in water, the shade becoming more red and deeper with increasing CNS content. For the sol. complexes the partition coeff. between ether and water at the ordinary temp. is: Cr aq<sub>2</sub>X<sub>4</sub>, about 3.6; H[Cr aq<sub>2</sub>X<sub>4</sub>], about 9.4; H<sub>2</sub>[Cr aqX<sub>5</sub>], about 4; H<sub>3</sub>[CrX<sub>6</sub>], about 0.3. In the cases of the tri- and tetra- thiocyno complexes the values of the partition coeff. depend somewhat on the mode of prepn. of the compds., which probably points to the presence of mixts. of stereoisomerides, such as are to be expected from Werner's theory. The velocity of decompn. of the several complexes has been measured by estg. the concn. of the CNS ions by the coloration with Fe(NO<sub>3</sub>)<sub>3</sub>. In aq. soln., the stability of the hexathiocyno complex is almost independent of the reaction of the soln. The remaining complexes become more stable in acid soln. as their CNS content diminishes, while the reverse is the case in alk. soln. The trithiocyno complex is fairly stable in ethereal soln., in which the stability of the other complexes rapidly diminishes with the CNS content. The complexes are sensitive to light. Analytical methods for the estn. of the several complexes have been worked out. The hexa and penta complexes are first pptd. as quinoline salts, and their relative proportions in the ppt. are elucidated by estn. of the Cr and CNS contents. The tri and tetra complexes are removed from the filtrate by means of ether, when it is found possible to sep. them by fractionation and to det. their amts. by 2 Cr estus. Finally, Cr and thiocyanogen are titrimetrically estd. in the extd. aq. soln. and the content of mona and di complex can then be calcd. if the content of hexa-aquo complex is known. The latter is determined by pptn. as chrome alum with KHSO<sub>4</sub> and alc. The chrome-thiocyno complexes are slowly formed in solns. which contain the hexa-aquo-chrome ion and the CNS ion. At the ordinary temp., however, the stable state is not attained for some years. The chem. equil. between the various complexes and the CNS ion has been detd. in aq. soln. at 50° for 10 solns. The results of chem. analysis are confirmed by measurements of the electrolytic cond. The affinity of the Cr atom for the CNS ion in normal soln. is calcd. from the equil. constn. in the usual manner, and is found to be +3710 cal. for the first and -570 cal. for the last CNS group. Graphs are given showing the relationship between the complexity and the concn. of the CNS ion, from which the equil. in a soln. can be calcd. if the concns. of Cr and CNS are known.

J. C. S.

A sparingly soluble double salt of calcium ferrocyanide and calcium ferrite. G. GRUBE [with L. BRAUMEISTER AND E. LÄMLÉ]. *Z. anorg. allgem. Chem.* 112, 245-61 (1920).—When Prussian blue is decomposed with excess of Ca(OH)<sub>2</sub> into sol. Ca ferrocyanide and Fe(OH)<sub>3</sub>, a side reaction occurs, the Ca ferrocyanide combining with the Fe(OH)<sub>3</sub> and excess of Ca(OH)<sub>2</sub> to form a sparingly sol. white ppt. As this is only stable in presence of excess of Ca(OH)<sub>2</sub>, and is decomposed by water, with formation of Fe(OH)<sub>3</sub>, it could not be isolated for analysis. By estg. the quantity of Ca ferrocyanide pptd. from soln. by known quantities of ferric and Ca hydroxides, it was established that the constituents are present in the double salt in the proportion Ca<sub>2</sub>Fe(CN)<sub>6</sub>:2Ca(OH)<sub>2</sub>:4Fe(OH)<sub>3</sub>, and that the compd. probably consists of a double salt of Ca ferrocyanide and Ca ferrite, 2CaFe<sub>2</sub>O<sub>4</sub>·Ca<sub>2</sub>Fe(CN)<sub>6</sub>. The compn. was confirmed by detns. of the change of hydroxyl-ion concn. in a Ca(OH)<sub>2</sub> soln. caused by adding Fe(OH)<sub>3</sub> and Ca ferrocyanide. There is no evidence of the formation of Ca ferrite when

$\text{Fe}(\text{OH})_2$  is added to a satd. soln. of  $\text{Ca}(\text{OH})_2$ . When Ca ferrocyanide is added to the mixt., the hydroxyl-ion concn. falls, and there is a break in the curve at the point corresponding with the compn.  $\text{Ca}_3\text{Fe}(\text{CN})_6 \cdot 2\text{Ca}(\text{OH})_2 \cdot 4\text{Fe}(\text{OH})_2$ . J. C. S.

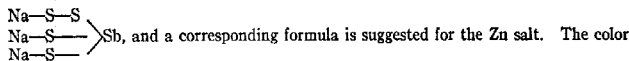
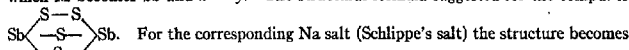
**Salts of stannic and plumbic acids.** HANS ZOCHER. *Z. anorg. allgem. Chem.* 112, 1-66(1920).—A study of stannates and plumbates was undertaken with the object of elucidating the so-called semi-colloidal state, with a critical discussion of which the paper opens. The methods for prepg. and analyzing alkali stannates are described.  $\text{Na}_2\text{SnO}_3$  crystallizes from NaOH solns. at ordinary temps. as the trihydrate,  $\text{Na}_2\text{Sn}(\text{OH})_6$ ; it is practically insol. in 7.0 N NaOH. When pptd. by NaOH at  $0^\circ$  or by alc. at  $0^\circ$ , or ordinary temps., it forms the tetrahydrate,  $\text{Na}_2\text{Sn}(\text{OH})_8 \cdot \text{H}_2\text{O}$ . The solubilities of the two hydrates were detd. between  $-5$  and  $50^\circ$ , that of the trihydrate, less sol. salt, which may be regarded as an "anhydride," diminishing with increasing temp., while that of the tetrahydrate increases. The transition point was difficult to det. by the dilatometric method, but from the soly. curves it appears to be close to  $-5^\circ$ . The trihydrate forms a eutectic with water at  $-11^\circ$ , the tetrahydrate at  $-7^\circ$ . In addition, a third hydrate, approximating to  $\text{Na}_2\text{Sn}(\text{OH})_8 \cdot 18\text{H}_2\text{O}$ , was discovered, which has a transition point to the "anhydride" at  $1^\circ$ . The hydrolysis of  $\text{Na}_2\text{SnO}_3$  in aq. solns. was studied by means of potential measurements. In normal solns. the hydrolysis is about 2.7%, and appears to be complete at a dilution of 1/3000 N. In normal solns. of the stannate the extent of hydrolysis gradually increases with time. This phenomenon is discussed in connection with similar observations in the case of other colloidal solns. and of solns. of  $\text{SnClH}_4$ . There is no evidence of adsorption of alkali by  $\text{Na}_2\text{SnO}_3$  under any conditions. Li stannate forms an "anhydride,"  $\text{Li}_2\text{Sn}(\text{OH})_6$ , isomorphous with the Na salt, and also a dihydrate of this salt,  $\text{Li}_2\text{Sn}(\text{OH})_8 \cdot 2\text{H}_2\text{O}$ . The solubilities of both salts were detd. between  $28^\circ$  and  $80^\circ$ . The two curves are approximately parallel, the solubilities increasing with the temp.; the transition point could not be found, but is probably below  $100^\circ$ .  $\text{K}_2\text{SnO}_3$  forms an "anhydride,"  $\text{K}_2\text{Sn}(\text{OH})_6$ , and also a mono- and di-hydrate of this salt. The solubilities are greater than those of the Na and Li salts. In the course of a long discussion on the chemistry of  $\text{SnO}_2$  from the colloidal point of view, the following points are elucidated. The low crystn. velocity of the oxide, resulting from its slight soly., facilitates its assumption of the colloidal state. The "ageing" of the colloid is accelerated or retarded by various influences, particularly by accompanying salts in soln. Coagulation, that is the coalescence of the bounding surfaces of the colloidal particles in soln., is retarded by the electrostatic charge on the particles. The work was also extended to the plumbates. Na plumbate was prepd. by dissolving freshly pptd.  $\text{PbO}_2$  in small quantities at a time, in boiling concd. (8-10 N) NaOH soln. The salt is very sparingly sol. in this soln., and separates in crystals which appear to be isomorphous with  $\text{Na}_2\text{SnO}_3$ . Although the analyses of the crystals always showed excess of  $\text{Na}_2\text{O}$ , their compn. is taken to be  $\text{Na}_2\text{Pb}(\text{OH})_6$ . Li plumbate was also prepd. and appeared, from its cryst. form, to be isomorphous with the Na salt. The properties of plumbic acid are discussed from the colloidal point of view. J. C. S.

**The causticization of sodium sulfate.** BERNHARD NEUMANN AND ERNST KARWAT. Breslau. *Z. Elektrochem.* 27, 114-24(1921).—Measurements have been made of the soly. of CaO in aq. solns. of NaOH and of  $\text{CaSO}_4$  in aq. solns. of  $\text{Na}_2\text{SO}_4$  and the reaction  $\text{Na}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 = \text{CaSO}_4 + 2\text{NaOH}$  has been studied at several temps. The equil. has been attained from both sides. The equil. const.,  $K$ , detd. from soly. data for CaO and  $\text{CaSO}_4$ , has at  $18^\circ$  a value  $(\text{OH})^2/(\text{SO}_4) = 0.388$ . It has been ascertained that the displacement of the equil. with temp. is in accordance with the van't Hoff equation of the reaction isochore. At  $40^\circ$   $K = 0.317$ , i. e., the OH concn. decreases with increase in temp. The calcd. values for the equil. const. agree fairly well with

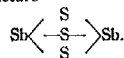
those detd. by expt., the deviations being due to dissociation behavior and not to the formation of double salts. The yield of NaOH decreases with increase in both the concn. of the starting materials and the temp. At ordinary temp. the max. conversion amounts to 60% and at 100° to 27%, the resulting NaOH being very dil. (7–2.7 g. per l.). With concd. solns. of the starting materials the conversion drops to but 10%. On evapg. the dil. solns. of NaOH a retrograde conversion sets in. In view of the above it is not likely that the process will be of any technical importance.

H. J. C.

**Antimony pentasulfide (sulfur auratum).** P. KIRCHHOFF. *Z. anorg. allgem. Chem.* 112, 67–80(1920).—The ordinary golden Sb sulfide is described in the literature as consisting of a mixt. of pentasulfide and trisulfide, with more or less free S. The purest form of the substance contains about 8% of S, which can be extd. with CS<sub>2</sub> or acetone, the residue having a compn. corresponding with the formula Sb<sub>2</sub>S<sub>4</sub>. This form is obtained by the action of dil. acids on Schlippe's salt, according to the equation  $2\text{Na}_3\text{SbS}_4 + 6\text{HCl} \rightarrow \text{Sb}_2\text{S}_4 + \text{S} + 6\text{NaCl} + 3\text{H}_2\text{S}$ . It is shown in the present paper that Sb<sub>2</sub>S<sub>4</sub> has no existence, but that golden Sb sulfide is a mixt. of Sb<sub>2</sub>S<sub>4</sub> with from 0 to 50% Sb<sub>2</sub>S<sub>3</sub> and a varying amt. of free S, according to the method of prepn. The compd. Sb<sub>2</sub>S<sub>4</sub> has been prepd. in a pure state from Zn thioantimonate. The latter salt, Zn<sub>3</sub>Sb<sub>2</sub>S<sub>6</sub>, was prepd. by the interaction of Schlippe's salt and ZnCl<sub>2</sub>. It formed a chrome-yellow ppt., which had a bright orange-red color when dried and ground. The crude substance contained about 6.7% of extractable S, and after removal of this, its compn. corresponded exactly with the above formula. The Zn thioantimonate is decomposed by dil. acids according to the equation  $\text{Zn}_3\text{Sb}_2\text{S}_6 + 6\text{HCl} \rightarrow \text{Sb}_2\text{S}_4 + 3\text{ZnCl}_2 + \text{H}_2\text{S}_2 + 2\text{H}_2\text{S}$ . Analysis of the orange-red residue from this reaction showed it to have the compn. Sb<sub>2</sub>S<sub>4</sub>, the same as that of the pure extd. orange form of golden Sb sulfide. The sulfide Sb<sub>2</sub>S<sub>4</sub> is to be regarded as a special case of compds. of the type M<sub>x</sub>(SbS<sub>4</sub>)<sub>y</sub>, in which M becomes Sb and x = y. The structural formula suggested for the compd. is



of the compd. Sb<sub>2</sub>S<sub>4</sub> and of the thioantimonates of the heavy metals is attributed to the presence of closed ring systems in the structure of these compds. The Na salt, in which there is no closed ring, is colorless. The red Sb<sub>2</sub>S<sub>3</sub> probably has the structure



J. C. S.

**The decomposition of persulfuric acid.** HERMAN PALME. *Z. anorg. allgem. Chem.* 112, 97–136(1920).—The rate of decompn. of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in solns. of 5.0, 7.53, and 10 N H<sub>2</sub>SO<sub>4</sub> at 50° has been studied. Since the reaction proceeds through the stages, H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> → Caro's acid → H<sub>2</sub>O<sub>2</sub>, it was necessary to develop a method for estg. these substances when all were present in the same soln. Advantage was taken of the fact that Caro's acid reacts immediately with KI, while H<sub>2</sub>O<sub>2</sub> reacts much more slowly, and H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> slowest of all. A sample of the soln. is mixed with KI and titrated rapidly with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, the time taken being noted, so that a correction can be applied for the small quantity of I liberated by the H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. The quantity of Caro's acid is thus found. A second sample is then treated with KI and titrated with Na<sub>2</sub>SO<sub>3</sub>, which reduces H<sub>2</sub>O<sub>2</sub>. This second titration gives the sum of Caro's acid and H<sub>2</sub>O<sub>2</sub>. Finally, the H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> is estd. in a third sample by adding the calcd. quantity of Na<sub>2</sub>SO<sub>3</sub> to reduce the other two compds. and estg. the H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> by the FeSO<sub>4</sub>-KMnO<sub>4</sub> method. The dilution

for the titrations corresponded with 2.0 g. of  $K_2S_2O_8$  per l., of which 200 cc. were titrated at a time. The expts. showed that, within the limits of error, the two reactions,  $H_2S_2O_8 + H_2O \xrightarrow{k_1} H_2SO_4 + H_2SO_4$  and  $H_2SO_8 + H_2O \xrightarrow{k_2} H_2O_4 + H_2SO_4$ , can be regarded as unimol. and irreversible. With increasing concn. of  $H_2SO_4$ , both velocity-consts. increased at a greater rate than the acid concn., but the ratio  $k_1/k_2$  remained const., 39.8. No relation between  $H^+$  concn. and velocity of reaction could be discovered, and the conclusion of Levi and Migliorini (*C. A.* 1, 1945) that undissociated  $H_2S_2O_8$ , the presence of which would be favored by increasing  $H^+$  concn., is less stable than its salts, was not confirmed. The expts. were not carried far beyond the time after which O begins to be evolved, through the reaction  $H_2S_2O_8 + H_2O_2 = 2H_2SO_4 + O_2$ , but it was shown that the velocity of this reaction increases considerably with decreasing concn. of acid. Friend's results (*J. Chem. Soc.* 89, 1092(1906)), which showed that the reaction is unimol., can be explained on the assumption that Caro's acid is first formed from  $H_2S_2O_8$ , and then reacts with  $H_2O_2$ .  $H_2S_2O_8$  probably does not itself react with  $H_2O_2$ . J. C. S.

**Photochemical decomposition of potassium cobaltizolate and its catalysis by neutral salts.** F. M. JÄGER AND G. BERGER. *Proc. Acad. Sci. Amsterdam* 23, 84-94 (1920).—The reduction of  $K_3Co(C_2O_4)_3$  by action of light according to  $2K_3Co(C_2O_4)_3 = 2CoC_2O_4 + 3K_2C_2O_4 + 2CO_2$  was studied at 21-3° with a quartz lamp as light source. The reaction velocity was found to be greater at smaller concns. but the total decompn. appeared to be independent of the original concn. Addition of EtOH had no appreciable effect but neutral salts, which included chlorides of K, Na, Li, Mg, Be and Fe<sup>++</sup>, accelerated the reaction, the acceleration reaching a max. at a certain concn. of each salt and diminishing with further addition of the salt. In some cases this diminution changed to a retardation and by  $MgCl_2$  the reaction could even be stopped. The maxima were found to lie at smaller concns. the greater the valency of the cation; the more rapidly does the acceleration decrease after reaching a max. the lower the concn. at the max. The sp. properties of the cation appear to play a part as well as its elec. charge since for LiCl, NaCl and KCl the maxima were found at concns. 1.65, 1.88 and 1.96 N, resp. A. R. MIDDLETON

**Chemical individuality of sulfur dichloride.** MAX BERGMANN AND IGNAZ BLOCH. *Ber.* 53B, 977-9(1920); cf. *C. A.* 14, 3414.—The formation of trisulfides of BzOH and of anisic acid by the action of  $SCl_2$  on the K salts of the thio-acids, with yields of 70-90% of the theory, affords strong proof of the individuality of  $SCl_2$  which has been much doubted. Were it a soln. of  $Cl_2$  or of  $Cl_2$  and  $SCl_4$  in  $S_2Cl_2$ , it should react with BzOK to form chiefly Bz tetrasulfide (m. 83-4°) and Bz disulfide (m. 136° approx.). While an equimol. mixt. of the two would indicate analytically a trisulfide, such a mixt. should melt irregularly at about 76-7° and upon repeated soln. its m. p. should change; the trisulfide obtained m. sharply at 165° and its compn. was not changed by fractional soln. or pptn. Artificial mixts. of di- and tetrasulfides were prepd.; the liquefaction of these extended 76° above 100°; recrystn. from a mixt. of  $CHCl_3$  and petroleum ether gave speary plates melting like the mixt.; repeated recrystn. caused a slow rise of melting interval and change of compn. toward the disulfide. A. R. MIDDLETON

**Preparation and properties of sodium amide.** J. M. MCGEE. *J. Am. Chem. Soc.* 43, 586-91(1921).—The  $NaNH_2$  was prepd. from pure Na and anhydrous liquid  $NH_3$ , with Pt gauze as a catalyst, in the container in which it was to be investigated, and never came in contact with air or moisture. It is a white cryst. solid, m. 208°, with a sp. cond. of  $1.665 \pm 0.005$  mho. at 210° with Pt electrodes. The cond. increases with increasing temp. (1.684, 1.718, 1.732 at 220°, 230° and 240°, resp.) but the results are only qual. as the  $NaNH_2$  decomps. to some extent; when it was cooled down to 210° again the cond. was only 1.375 mho. The fused  $NaNH_2$  has not as great a solvent action as reported by Titherley and others, whose preps. must have contained consider-

able NaOH. A glass vessel in which the  $\text{NaNH}_2$  was kept fused 14 hrs. at a temp. not above  $240^\circ$  was not attacked; after 2-3 days at  $270-300^\circ$ , however, it was slightly etched. The Pt black of the gauze catalyzer and the electrodes of the cond. cell were not only slowly dissolved but the Pt at the same time catalyzed the decompn. of the  $\text{NaNH}_2$ . The decompn. is slow at  $210^\circ$  but increases rapidly with the temp. The gas evolved has the odor of  $\text{NH}_3$  and is completely absorbed by concd.  $\text{H}_2\text{SO}_4$ , so cannot contain appreciable amts. of N or H. The residue is either Na imide or nitride for on decompn. with alc. and  $\text{H}_2\text{O}$  it gives  $\text{NH}_3$  only and no H. No blue solns. of Na in fused  $\text{NaNH}_2$  could be obtained, as stated by Titherley. C. A. R.

**Production of high-grade arsine and its quantitative estimation.** H. THOMS AND L. HESS. *Ber. pharm. Ges.* 30, 483-9(1921).—A Ca arsenide (cf. Lebeau, *Ann. chim. phys.* [7] 25, 478; and Moissan, *Compt. rend.*, 127, 584) was prepd. by the interaction of shredded Ca (2.4) and powdered As (3.1) dild. with fine quartz sand (5.5) in a suitable Fe container. The resulting product was thereupon used in powdered form as a diluent with further quantities of the Ca-As mixt. in producing a more concd. form of the arsenide, which on examn. yielded about 14 and 0.004 vol. %  $\text{AsH}_3$  and H, resp. As an absorption medium for  $\text{AsH}_3$ ,  $\text{CuCl}_2$  was used in preference to  $\text{AgNO}_3$  soln. The decompn. of  $\text{AsH}_3$  in aq. soln. was studied, such solns. being susceptible of titration in 2 phases. Thus, to the neutral soln. 0.01 N I soln. is added, whereupon the following reaction takes place:  $\text{AsH}_3 + 6\text{I} + 3\text{H}_2\text{O} = \text{H}_3\text{AsO}_3 + 6\text{HI}$ .  $\text{K}_2\text{CO}_3$  soln. is now added whereby decolorization is effected. The titration is then effected in the usual way to the formation of  $\text{H}_4\text{AsO}_4$ . W. O. E.

**Fractional precipitation** (JOLIBOIS, *et al.*) 2. Separation of two salts having a common ion (SCHLOESING) 2. The influence of copper on the rate of solution of iron in acids (BELL, PATRICK) 2. A new calcium salt (GAUCHER, ROLLIN) 10.

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## 7—ANALYTICAL CHEMISTRY

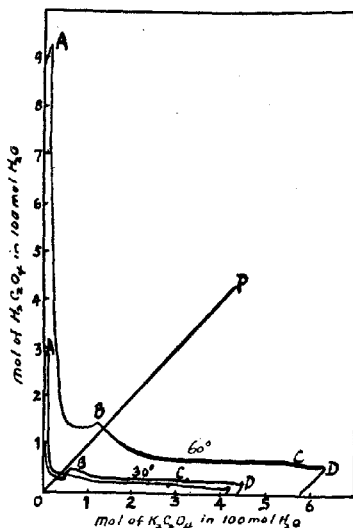
WILLIAM T. HALL

The determination of bases, combined with weak or moderately strong acids, and of very weak bases with acids and vice versa. I. M. KOLTHOFF. *Z. anorg. allgem. Chem.* 115, 168-80(1921).—It is shown theoretically and proved by expt. that with Tropaeolin O, acids and bases having dissociation consts. greater than  $10^{-10}$  can be titrated with 1% accuracy, while salts of moderately weak acids (or vice versa) having a dissociation const.  $\leq 10^{-4}$  can also be titrated. Exptl. data are given for the Na salts of  $\text{AcOH}$ ,  $\text{BzOH}$ , formic, and salicylic acids, and for aniline, urotropine, boric acid, and phenol. A. F. KAUFER

**Indicator properties of two new phthaleins.** (1,2,3-xylenolphthalein and *o*- $\alpha$ -naphtholphthalein). WILHELM CSÁNYI. *Z. Elektrochem.* 27, 64-9(1921).—It is shown that 1,2,3-xylenolphthalein can be regarded as an "alkaline analog" of Me orange in the sense employed by Bjerrum (cf. *C. A.* 11, 2759). At higher  $\text{OH}^-$  concns. this indicator exists in the colored or quinoid form. The indicator gives the following colors at the indicated  $\text{H}^+$  concns.:  $10^{-8.7}$  colorless,  $10^{-8.5}$  pale blue,  $10^{-8.1}$  blue,  $10^{-10.1}$  deep blue. The titration exponent lies at  $p_{\text{H}} = 9.7$  (i. e., at  $[\text{H}^+] = 10^{-9.7}$ ). In contrast to 1,2,3-xylenolphthalein, *o*- $\alpha$ -naphtholphthalein assumes the colorless or carbinoloid form at higher OH concns. Its acid color is yellow or olive green; its alkaline color is deep green which becomes colorless on standing, owing to conversion into the carbinoloid form. The titration exponent of this indicator lies at  $p_{\text{H}} = 11.5$ .

H. JERMAIN CREIGHTON

**Potassium binoxalate as a standard in alkalimetry.** YUKICHI OSAKA AND KINJI ANDO. *J. Tokyo Chem. Soc.* **41**, 945-51 (1920).—Although  $\text{KHC}_2\text{O}_4$  crystallizes out in anhydrous form above  $15^\circ$ , the ordinary method of purification does not produce a sufficiently reliable substance for use as a standard in alkalimetry. Recalcg.



the data given by Koppela and Cahn (cf. *C. A.* **3**, 327), O. and A. plotted an equil. curve by use of which pure anhydrous  $\text{KHC}_2\text{O}_4$  can easily be prepd. In the figure,  $AB$  represents the soly. curve of  $\text{K}$  tetraoxalate,  $BC$   $\text{KHC}_2\text{O}_4$ , and  $CD$   $\text{K}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . The line  $OP$  represents the points at which  $\text{K}_2\text{C}_2\text{O}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$  are present in equimol. ratio. The condition for formation of anhydrous  $\text{KHC}_2\text{O}_4$  must be along  $OP$  between  $40$  and  $60^\circ$ . Exptl. data are given to show how easily anhydrous  $\text{KHC}_2\text{O}_4$  can be obtained by this procedure. The method is as follows: The curve shows that at  $60^\circ$  in 100 mols.  $\text{H}_2\text{O}$ , there are 1.1 mols. of  $\text{H}_2\text{C}_2\text{O}_4$  and 1.5 mols. of  $\text{K}_2\text{C}_2\text{O}_4$ . Thus 80 g. of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and 160 g. of  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  are placed in a large Erlenmeyer flask, and to it a convenient amt.

of equimol. soln. of the 2 salts is added and then  $(1000 - \text{H}_2\text{O of crystn.})$  cc. of  $\text{H}_2\text{O}$  is added. The flask is corked with a small opening, and is heated at the temp. between  $25$  and  $60^\circ$  and allowed to cool to about  $25^\circ$ . The ppt. is filtered, washed with  $\text{H}_2\text{O}$  (at  $50^\circ$ ) and dried. The resulting product is  $\text{KHC}_2\text{O}_4$  without any  $\text{H}_2\text{O}$  of crystn. S. T.

**The De Roode-perchloric acid method for determining potash.** T. E. KERR. *J. Ind. Eng. Chem.* **12**, 276-7 (1920).—Sulfates,  $\text{NH}_3$  and org. matter must be removed.  $\text{KClO}_4$  is produced and pptd. by cold alc. and collected on a filter, which is then dried, weighed and washed with hot  $\text{H}_2\text{O}$ , and then reweighed. The loss in wt. =  $\text{KClO}_4$  and is calcd. into  $\text{K}_2\text{O}$  by the factor 0.34. The results justify further study of this process which eliminates costly  $\text{PtCl}_4$ . JEROME ALEXANDER

**The determination of calcium in the presence of phosphates.** J. F. BREAZHALE. *J. Assoc. Off. Agr. Chem.* **4**, 124-34 (1920).—The soly. of  $\text{CaC}_2\text{O}_4$  was detd. in hot and  $\text{O}_4$  cold solns. of  $\text{H}_2\text{C}_2\text{O}_4$ ; in solns. of  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{S}$  in presence of  $\text{H}_2\text{C}_2\text{O}_4$ ; and in pure solns. of the same salts at the temp. of the boiling solns. and at room temp. The results obtained in these detns. and in the coöperative analyses of prepd. samples show that the method of detg.  $\text{Ca}$  in the presence of phosphates by pptn. with dil.  $\text{H}_2\text{C}_2\text{O}_4$  gives accurate results and is particularly well suited to the detn. of  $\text{Ca}$  in the analysis of plant ash. W. H. ROSS

**Electrolytic determination of copper in iron pyrites and roasted pyrite.** R. MÜLLER. *Chem.-Ztg.* **45**, 135-6 (1921).—In criticism of the article by Mengler (*C. A.* **14**, 3383), the enormous expense of  $\text{Pt}$  in Germany to-day is pointed out. It is also claimed that Mengler recommends an elec. current of higher potential than is actually necessary. The double electrolysis of the  $\text{Cu}$  is criticized. It is suggested that Mengler has mis-

taken CuS for Pb in the cathode deposit and that other organic substances may be used instead of citric acid to reduce anodic polarization.

W. T. H.

**Electrolytic determination of copper in iron pyrites and roasted pyrite.** E. MENOGER. *Chem.-Ztg.* 45, 136(1921).—In reply to the above criticism, it is stated that the recommended potential of the elec. current has been found useful, that Pb actually does deposit on the cathode with Cu because of the presence of citric acid in the bath, and that other organic acids in place of citric acid have not proved as suitable.

W. T. H.

**Silicon in cast iron.** B. R. RUSSELL. *Eng. Mining J.* 109, No. 7; *Bol. miner.* 9, 617-23.—A discussion of the relative merits of various methods of analysis.

L. E. GILSON

**The analysis of commercial zincs.** E. OLIVIER. *Ann. chim. anal. chim. app.* 2, 199-207, 226-34(1920).—The methods used at Vieille-Montagne during the last 30 yrs. are described in detail showing how each reagent and standard soln. is prepd., as well as the technic of the analytical operations, including sampling. The detns. of Pb, Fe, Cd, Cu, Sb, As and Sn are discussed.

A. J. SALATHE

**Detection of manganese in the presence of phosphates.** T. SABALITSCHKA AND W. ERDMANN. *Ber. pharm. Ges.* 30, 443-5(1920); cf. Wester, *C. A.* 14, 2599, 2897, and Schmidt, *C. A.* 14, 2897.—The author shows by expt. that the detection of Mn is rendered difficult if not impossible through the presence of relatively large quantities of Ba phosphate in Schmidt's scheme of sepn.

W. O. E.

**Opalescence in the estimation of minute quantities of chlorides.** STICH. *Pharm. Ztg.* 65, 1009(1920).—The opalescence arising from the addition of  $\text{AgNO}_3$  to aq. solns. containin gtraces of Cl is made the basis for quant. detn. in connection with a colorimeter.

W. O. E.

**Comparative results with Scales' method and Devarda's alloy for reducing nitric nitrogen.** ARTHUR P. HARRISON. U. S. Dept. Agr., Bur. Plant Ind. *J. Biol. Chem.* 46, 53-6(1921).—"The reduction of nitrates by a Zn-Cu couple as suggested by Scales (*C. A.* 11, 461) is as reliable as by Devarda's alloy (*Z. anal. Chem.* 33, 113), is more convenient, and, as no weighing of reagents is necessary, the detn. may be completed sooner. A regular Kjeldahl rack and condenser may be used instead of the special app. described by Scales. After the Zn-Cu couple has been used it may be rinsed and left in the flask for the next detn. and the Zn may be used without renewal for several months. For use, 150 cc. of the  $\text{CuSO}_4$  soln. are left over the metal for 10 min., rinsed once with cold  $\text{H}_2\text{O}$ , the sample poured in, a roughly measured 6-g. quantity of a 5:1 mixt. of NaCl and  $\text{MgO}$  added, and the distn. carried out. The detn. is completed according to the technic of Scales and Harrison (*C. A.* 14, 1591).

A. P. LOTHROP

**The detection of volatile alkylamines in the presence of ammonia and of volatile tertiary alkylamines in the presence of volatile primary and secondary alkylamines.** H. E. WOODWARD AND C. L. ALSBERG. U. S. Dept. Agr., Bur. Chem. *J. Biol. Chem.* 46, 1-7(1921).—If  $\text{HCHO}$  is allowed to react in a soln. containing both  $\text{NH}_3$  and amines, the  $\text{NH}_3$  is converted into such compds. as hexamethylenetetramine and the amine will cause a certain amt. of  $\text{HCO}_2\text{H}$  to be produced from the  $\text{HCHO}$  and thus the formation of  $\text{HCO}_2\text{H}$  indicates the presence of amines in the soln. under examn. The  $\text{HCO}_2\text{H}$  is detected by means of  $\text{HgBr}_2$ , which is reduced to white insol.  $\text{HgBr}$ . Compds. of  $\text{NH}_3$ , and mono- and dimethylamine with  $\text{HgBr}_2$  are sol. in excess of  $\text{HCHO}$ . To detect volatile alkylamines in the presence of  $\text{NH}_3$  proceed as follows: Sep. the volatile alkali by distn. or aeration into a slight excess of acid. Evap. to small vol., transfer to a small flask, make alk. with NaOH and distil into about 1 cc. of 40%  $\text{HCHO}$  in a test-tube. Add about 1 cc. of reagent (18 g.  $\text{HgBr}_2$  and 12 g.  $\text{KBr}$  in 100 cc. of  $\text{H}_2\text{O}$ ) and warm



slightly in a steam bath. In the presence of 0.5 mg. of amine N a fine white ppt. of HgBr appears and with larger amts. there is a heavy ppt. even before heating. The reaction is roughly quant. within a certain range of concn. of the solns. If 10 cc. of amine soln. is between 0.01 and 0.02 N and 1 cc. of HCHO is used, the wt. of the HgBr ppt. is nearly 20 times the wt. of the amine N. A nephelometer is useful with small amts. To test for *trimethylamine* sep. the volatile alkali by distn. or aeration into a slight excess of acid, using Me red as indicator. Evap. the acid soln. to small vol., filter if necessary, and transfer to a small flask. Add Mayer's reagent (45 g. HgI<sub>2</sub> and 33 g. KI in 100 cc.) from a graduated pipet or buret until pptn. is complete. 1 cc. of reagent ppts. 59 mg. of trimethylamine. The compd. formed has the formula, (CH<sub>3</sub>)<sub>3</sub>N.HI.HgI<sub>2</sub> and trimethylamine may be recovered from it by dissolving the crystals in NaOH and Na<sub>2</sub>S and distg.; in this manner trimethylamine may be freed from traces of mono- and dimethylamine. The reagent does not give a ppt. with salts of NH<sub>4</sub> or of monomethyl- or monoethylamine. Salts of dimethyl- and diethylamine are also pptd. from solns. of considerable concn.; if 1 cc. of soln. contains more than 20 mg. of diethyl- or more than 4 mg. of dimethylamine, pptn. occurs. Solns. of trimethylamine as dil. as 0.01 N slowly sep. long yellow needles and in 0.1 N solns. a heavy yellow ppt. forms immediately. Triethylammonium chloride behaves in a similar manner. The limit of the test is about 3 mg. of trimethylamine in 5 cc. As little as 0.5 mg. may be detected by adding only a few drops of Mayer's reagent and shaking out the mixt. in a separatory funnel with a mixt. of equal parts of CHCl<sub>3</sub> and AcOEt; on evapn. of the ext. the yellow color of the amine compd. can be readily distinguished in the residue from the red HgI<sub>2</sub>. These methods are especially useful in testing for volatile alkylamines in foodstuffs where their presence may be regarded in most instances as an index of decompn. The prepn. and properties of methyl- and ethylammonium mercuric iodides have recently been described by Jamieson and Wherry (*C. A.* 14, 1323).

A. P. LOTHROP

**Minor laboratory notes.** VLADIMIR NJEGOVAN. *Chem.-Zig.* 45, 141-2(1921).—In place of Pt wire or of magnesia rods (Wedekind, *C. A.* 6, 1413) N. uses for the *microcosmic salt bead test* graphite rods from lead pencils. These do not work well with the borax bead. For *flame tests* N. uses strips of filter paper. These if allowed to char give Na and Ca flames. For the flame test a tiny glass flask with a piece of Zn, some HCl and a little of the soln. being tested is held with its mouth to the air hole of a Bunsen burner. The flame is colored with 1 drop of N NaCl, or with 2-3 drops of N alk. earth chloride. With K and Cu the method does not succeed. The graphite rods may be used also for the Co test for Al or Zn.

J. J. MORGAN

Production of arsine and its estimation (THOMS, HESS) 6. Radiology applied to the testing of materials (FLEMING, CLARK) 3.

STADLIN, W.: Die störenden Einflüsse auf das Eintreten und die Eindeutigkeit analytischer Reaktionen. Leipzig: Verlag von Georg Thieme. 70 pp. M. 9, foreign price M. 18.

**Indicator.** M. TSUJI. Japan 36,115, Apr. 8, 1920. Eleven g. of the dry inside skin of *Alunus tinctoria*, Koidz., are mixed with 100 g. 1% AcOH, set aside for 24 hrs., filtered, neutralized with 0.6 g. Na<sub>2</sub>CO<sub>3</sub>, mixed with 0.5 g. Fe sulfate and filtered. The soln. is colorless when acid and red when alk. The coloring matter is obtained in powder form and is used instead of litmus or phenolphthalein.

## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND WALTER F. HUNT

**Owyheeite.** EARL V. SHANNON. U. S. Nat. Mus. *Am. Mineral* 6, 82-3(1921).—This mineral had been previously described as "silver-jamesonite" (*C. A.* 15, 40) but is now believed to be distinct and is named after the locality. Recalc. of the formula from the analysis gives:  $(\text{Ag,Cu})_2\text{S}_{1.5}(\text{Pb,F c})\text{S}_{3.5}\text{Sb}_2\text{S}_3$ , or essentially  $\text{Ag}_2\text{Pb}_4(\text{Sb}_2\text{S}_3)_1$ .

E. T. W.

**The affinity of the aragonite-calcite transformation.** HANS L. J. BÄCKSTRÖM Stockholm. *Z. physik. Chem.* 97, 179-228(1921).—Detns. have been made of the soly. of Iceland spar and synthetic aragonite in  $\text{H}_2\text{O}$  in the presence of  $\text{CO}_2$  at definite pressures, and the following values obtained for aragonite and calcite, respectively: 1.46 and 1.30 g. per l. at  $9^\circ$  and 777 mm.  $\text{CO}_2$  pressure, 1.066 and 0.943 g. per l. at  $25^\circ$  and 762 mm.  $\text{CO}_2$  pressure, 0.876 and 0.765 g. per l. at  $35^\circ$  and 744 mm.  $\text{CO}_2$  pressure. It has been found that the soly. is influenced by the size of the grain. The velocity curves for Iceland spar, as well as those for aragonite at the lowest temps., show that there exists in the neighborhood of the equil. a distinct region in which the reaction velocity is practically zero. With pulverized Iceland spar it has been observed that during the course of expts. with the same material the reaction velocity decreases continuously. It has been concluded, therefore, that in this case the Noyes-Nernst law for reaction velocity in heterogeneous systems does not hold. The following values have been found for the affinity,  $A = 3RT\ln[\text{Ca}^{++}]_{\text{aragonite}}/[\text{Ca}^{++}]_{\text{calcite}}$ : 160 cal. at  $9^\circ$ , 191.3 cal. at  $25^\circ$  and 220.6 cal. at  $35^\circ$ . The transformation temp. of aragonite into calcite has been calcd. to be  $-43^\circ \pm 5^\circ$ , and the heat of transformation  $-670$  cal. ( $\pm 100$ ). The transformation temp. increases  $1^\circ$  per 40 atms. For this reason pure aragonite is never found in nature as the stable form. In conclusion the results of previous investigations are discussed.

H. JERMAIN CRIGHTON

**The etching figures of topaz.** ARTHUR P. HONESS. Princeton Univ. *Am. Mineral.* 6, 71-7(1921).—Topaz crystals have been etched by immersion for a few min. in fusions of KOH and of  $\text{KHSO}_4 + \text{CaF}_2$ . The figures produced on various forms all agree in indicating that the symmetry of the mineral is orthorhombic-holohedral.

E. T. W.

**Trigonite and dixenite, two new minerals from the Langbanshyttan mines.** GUSR. FLINK. *Geol. För. Förh.* 42, 436-52(1920).—[Swedish with English summary.]—The name *trigonite* is from the Greek *trigonos*, triangle, referring to the crystal habit. The physical properties of the mineral are: Color pale yellow to brownish; luster vitreous to adamantine.  $H = 2$  to  $3$ ; sp. gr. 8.28. Cleavage perfect on  $b$  (010), less perfect on  $p$  (101). Observed only in crystals, up to  $1/2$  cm. in diameter, usually markedly triangular in outline. Monoclinic, domatic,  $a:b:c = 1.0740:1:1.6590$ ,  $\beta = 91^\circ 31'$ . Forms:  $a(100)$ ,  $b(\bar{1}00)$ ,  $c(001)$ ,  $d(00\bar{1})$ ,  $e(010)$ ,  $p(101)$ ,  $q(\bar{1}0\bar{1})$ ,  $r(10\bar{1})$ ,  $s(\bar{1}01)$ ,  $f(011)$ ,  $g(012)$ ,  $h(014)$ ,  $i(01\bar{1})$ ,  $m(110)$ ,  $k(\bar{1}10)$ ,  $l(210)$ ,  $n(111)$ , and  $o(11\bar{1})$ . The dominant forms are  $e$ , forming the base of the apparent triangular prism, and  $c$ ,  $q$  and  $r$  forming the sides of the same (the plane of symmetry crossing the center of this prism).  $\alpha = 2.08$  and  $\gamma = 2.16$ , both  $\pm 0.02$ , determined by N. Alsén by immersion in mixts. of S and Se. Double refraction 0.06; optic axial plane  $b(010)$ ; extinction angle in this plane  $45^\circ$ . Non-pleochroic. The mineral dissolves readily in dil. acids. Analysis was made on several small samples by Dr. R. Mauzelius, giving average values:  $\text{As}_2\text{O}_3$  28.83,  $\text{PbO}$  63.40,  $\text{CaO}$  0.23,  $\text{FeO}$  0.15,  $\text{MnO}$  6.79,  $\text{MgO}$  0.11,  $\text{H}_2\text{O}$  0.81, Cl trace insol. 0.13, sum 100.45%. The scarcity of the material prevented quant. detn. of the state of oxidation of the As, but the indications point to the arsenious form. The formula derived is  $\text{H}_2\text{O} \cdot 2\text{MnO} \cdot 0.6\text{PbO} \cdot 3\text{As}_2\text{O}_3$  or  $\text{HMnPh}(\text{AsO}_3)_3$ , which requires  $\text{H}_2\text{O}$  0.9,  $\text{MnO}$  6.7,  $\text{PbO}$  64.0, and  $\text{As}_2\text{O}_3$  28.4%

It was found in 1919 at the 150 meter level in masses of dolomite, associated with native Pb and several undetd. minerals. This mineral is interesting as adding one to the very small group of minerals crystg. in the monoclinic-domatic (clinohedral) class; it is noteworthy that one other representative of this class, tilasite, also occurs at Långban, and another, clinohedrite, in the similar deposit at Franklin Furnace, N. J. [The species may be regarded as satisfactorily established, although the formula is perhaps open to some modification.—Abstr.] The name *dixenite* is from Greek *di* = two and *xenos* = stranger, referring to the unique association of  $\text{SiO}_2$  and  $\text{As}_2\text{O}_3$  in a compd. Its physical properties are: Color nearly black, but intense red by transmitted light when in thin sheets; luster metallic to resinous.  $H = 3$  to 4; sp. gr. = 4.20. Cleavage basal, micaceous. Observed only as aggregates of thin flakes without crystal outlines. X-ray study shows the symmetry to be hexagonal or rhombohedral. Mean  $n = 1.96 \pm 0.02$ . Under the microscope uniaxial and positive. Non-pleochroic. The mineral dissolves readily in HCl with the sepn. of gelatinous  $\text{SiO}_2$  and in  $\text{HNO}_3$  with evolution of brown fumes, indicating the As to be trivalent. Analysis by Mauzelius on a small amt. of material gave:  $\text{As}_2\text{O}_3$  30.55,  $\text{P}_2\text{O}_5$  0.09,  $\text{SiO}_2$  8.66,  $\text{CuO}$  3.38,  $\text{FeO}$  4.54,  $\text{MnO}$  48.94,  $\text{MgO}$  0.50,  $\text{CaO}$  0.28,  $\text{H}_2\text{O}$  3.38, sum 100.32%. This corresponds to  $4\text{RO} \cdot \text{SiO}_2 \cdot \text{As}_2\text{O}_3$ , or, representing all the R by Mn and the water as hydroxyl,  $(\text{MnOH})_2\text{Mn}_2(\text{SiO}_3)(\text{AsO}_3)_2$ , which would require  $\text{H}_2\text{O}$  2.8,  $\text{MnO}$  56.2,  $\text{SiO}_2$  9.6, and  $\text{As}_2\text{O}_3$  31.4%. Found like the preceding mineral, but in hematite and serpentine as well as dolomite. [May be regarded as established, except that the formula is somewhat uncertain.—ABSTR.] E. T. W.

**Paternoite**, a new mineral from the salt-bearing deposit at Monte Sambuco, Calascibetta, Sicily. F. MILLOSEVICH. *Rend. accad. Lincei, phys. math. and nat. sci. class 29*, 286-9 (1920).—The name is in honor of Emanuele Paternò. Its physical properties are: Color pure white; structure minutely granular; somewhat deliquescent. Sp. gr. 2.11. Under the microscope seen to be made up of minute cryst. laminas of rhombic outline, with acute angle about  $62^\circ$ , rarely truncated and hexagon-like. Mean  $n$  by immersion method is about 1.475. Extinction symmetrical. It is partially sol. in  $\text{H}_2\text{O}$ , giving an alk. reaction. Readily sol. in dil. acids. The material was dried at  $100^\circ$ , water lost below this temp. being considered hygroscopic, as the optical properties are constant up to this point. The B was detd. by Gooch's method, the  $\text{H}_2\text{O}$  by the PbO method. The results were:  $\text{B}_2\text{O}_3$  66.02,  $\text{MgO}$  10.93,  $\text{K}_2\text{O}$  1.08,  $\text{Na}_2\text{O}$  0.36,  $\text{Cl}$  2.35,  $\text{SO}_3$  1.06,  $\text{H}_2\text{O}$  19.16, sum less O =  $\text{Cl}$  0.53, 100.43%. The K and Cl are believed to be present as admixed carnallite, the Na and  $\text{SO}_3$  as bloedite; on subtracting these, with the corresponding amts. of  $\text{MgO}$  and  $\text{H}_2\text{O}$ , the remainder is:  $\text{B}_2\text{O}_3$  71.66,  $\text{MgO}$  10.67,  $\text{H}_2\text{O}$  17.67%, corresponding fairly closely to  $\text{MgO} \cdot 4\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  or  $\text{H}_2\text{MgB}_4\text{O}_{17}$  (theory  $\text{B}_2\text{O}_3$  71.4,  $\text{MgO}$  10.3,  $\text{H}_2\text{O}$  18.3%). [This may provisionally be accepted as a new species, although more complete optical data and an analysis of purer material would be desirable. In particular, the  $\text{H}_2\text{O}$  content needs study, especially as to the rate of loss both below and above  $100^\circ$ .—ABSTR.] E. T. W.

**Bloedite and other minerals from the salt-bearing deposit at Monte Sambuco territory of Calascibetta, Sicily.** F. MILLOSEVICH. *Rend. accad. Lincei, Phys. Math. and Nat. Sci. class 29*, 344-7 (1920).—The deposit contains, besides kieserite, halite, etc., abundant bloedite in good crystals of which detailed measurements and an analysis are given. In the bloedite-bearing beds there are numerous small rounded masses of a new mineral (cf. preceding abstract), which was at first thought to be boracite. E. T. W.

**Notes and analyses of the Hermitage Plains aerolite.** HAROLD P. WHEAT. *Records Geol. Survey N. S. W.* 9, 108-9 (1920).—An analysis of the Hermitage Plains aerolite gave:  $\text{SiO}_2$  37.96,  $\text{Al}_2\text{O}_3$  2.95,  $\text{MgO}$  24.87,  $\text{CaO}$  2.86,  $\text{Na}_2\text{O}$  0.97,  $\text{K}_2\text{O}$  0.21,  $\text{Fe}$  19.19,  $\text{Ni}$  2.06,  $\text{Co}$  0.08,  $\text{CO}_2$  0.10,  $\text{SO}_3$  <0.01,  $\text{Cl}$  <0.01,  $\text{P}$  0.10,  $\text{FeS}$  4.05,  $\text{Cr}_2\text{O}_3$  0.29,

MnO 0.16,  $V_2O_5$  <0.01,  $H_2O$  (100°) 0.43,  $H_2O$  (above 100°) 1.81, O (by diff.) 2.41, sum 100%.

S. G. GORDON

**Hydrogen sulfide as a mineralizing agent.** E. CORRESE. *Rass. min.* 53, 82-4 (1920).—The deposition of metallic sulfides in veins is explained on the basis of soly. of the sulfides in  $H_2S$  water especially under pressure. When such solns. have penetrated limestones, the excess  $H_2S$  has interacted with the  $CaCO_3$  to form gypsum which was carried off in soln. The excess  $H_2S$  having been removed, the minerals were deposited in the voids formed by removal of the limestone. This explains the origin of masses of gypsum not associated with rock salt. Some S deposits have probably been formed similarly, as also Ba sulfate, the Ba being carried in soln. as a sulfide and subsequently oxidized.

J. S. LAIRD

**Deposits of sulfur containing bituminous substances in the mines of Huascama, Cerritos, San Luis Potosi, Mexico.** E. WYRICH. *Bol. minero* 9, 614-6 (1920).—The S as mined is dark colored but contains less than 1% of bituminous material. Some of the mine workings are more than 50 m. deep but no  $H_2S$  or  $SO_2$  has ever been found. This leads W. to believe that the S was not formed by the reaction between these gases as is usually the case, but that the deposit was formed by the condensation of S vapor forced up from below. The presence of large amts. of *anhydrite* mixed with the S lends support to this view.

L. E. GILSON

**The origin of natural fuels.** F. RIGAUD. *Rev. sci.* 58, 588-91, 619-26 (1920).—Arguments are brought forward in favor of the mineral theory and against the org. theory of the formation of petroleum, lignites, coal, etc. Just as the calorific value of the vegetable fuels found on the surface of the earth is due to stored up solar energy, so R. thinks that the calorific value of fuels found in the earth's crust is due to stored energy derived from the hot central core of the earth. In order that dead vegetable matter may be preserved for any length of time it must be placed under 1 of 3 sets of conditions: (a) Complete dessication and preservation in a perfectly dry atmosphere; (b) kept at a temp. of 10° or less; (c) kept in an antiseptic medium. None of these conditions were to be found at the period when, according to the org. theory, the coal beds were formed, except in a very few rare instances (Cologne lignite), as the temp. of the earth in the pre-glacial period was, in R.'s opinion, such as to cause very rapid decompn. of any dead vegetable material. In the case of peat bogs, vegetable remains are preserved by the combined action of cold and of various antiseptic substances which are formed by the partial decompn. of the vegetable material. But most of the mineral fuels are due to the action of fresh or salt water on the fused central core of the earth; the  $H_2O$  is decompd. and oxidizes the Fe, while the liberated H reacts with the C present in the molten Fe and forms various hydrocarbons. Part of the latter are solidified by various secondary reactions, and give rise to the coal beds. The liquid hydrocarbons percolate through the rocks, and collect in pockets or find their way to the surface of the earth. The gaseous hydrocarbons quite easily make their escape, and are found in many places, such as bogs, etc., and in gases from volcanoes; they are also found in mines, and though they have been especially noted in coal mines they are also present in other mines, and have been known to cause explosions in Fe and salt mines. The innumerable remains of fauna and flora to be found in coal beds are explained, not by the fact that the coal originated from them, but by the fact that they fell into the hydrocarbons when the latter were still in a fluid state and acted as antiseptics to preserve them.

A. P.-C.

Clay of Ancylius (Odén) 15. The elasticity constants of sylvite (FORSTERLING) 2.

**9—METALLURGY AND METALLOGRAPHY**

D. J. DEMOREST, ROBERT S. WILLIAMS

**Chloridizing and leaching as practiced in Sweden.** N. OSTMAN. *Eng. Mining J.* 111, 417-22(1921).—A description of a successful modern adaptation of the Longmaid-Henderson process. The pyrite cinder is roasted with 12 to 20% of NaCl in Ramón-Beskow furnaces. These are of the multiple-hearth type, with revolving central shaft, and are heated with producer gas made from tarry wood. The acid gases, which form in the lower compartment, are led to towers and condensed by water to give a strong acid (15 to 20 g. HCl per l.) for leaching. Chloridizing action begins on the second floor of the furnace, and here no outside heat is applied, so that the temp. does not go above 800°, and caking of ore and volatilization of Cu are avoided. Successful tests have been made on chloridizing roasted flotation concentrates carrying 7 to 8% Cu. In leaching, an innovation is the use of a "preleaching machine," in which the chloridized material is spread in a thin layer while still hot and treated with a limited amt. of water, which renders the anhydrous Na<sub>2</sub>SO<sub>4</sub> easily sol. and prevents the formation of the lumps which caused so much trouble in the old method of direct leaching. The use of this machine generates considerable steam, which is condensed to hot water for leaching, making additional steam usually unnecessary and also keeping the plant free from dust and escaped steam. From the machine the prep'd. ore goes to the leaching tanks, where the time of treatment is much shortened by the "pre-leaching." Pptn. is carried on in large closed revolving iron drums containing scrap Fe, a method which has many advantages over the old open method. Zn-bearing cinders are being treated in similar manner with Ramón-Beskow furnaces to obtain Zn solns. for the manuf. of lithopone. The spent purple ore is smelted for its Fe content, usually being first briquetted in improved Ramón tunnel furnaces. The briquets are run in on cars and heated to 1450°, a temp. which eliminates most of the remaining S during the briquetting. The furnaces have water-cooled supports and boxes to protect the cars from the flame.

A. BUTTS

**Tungsten in 1918.** FRANK L. HESS. U. S. Geol. Survey, *Mineral Resources of U. S., 1918*, Part I, 973-1026 (preprint No. 30, published Mar. 21, 1921). E. H.

**Tungsten.** JULIUS L. F. VOGEL. *Chem. Age* (London) 3, 308-9(1920).—This article gives the results of the experience of English manufacturers in establishing the manuf. of Fe-W and W powder. The raw materials are wolframite (including hübnerite) and scheelite. When associated with Sn ore the upper layers of W ore are the purer. The feebly magnetic properties of wolframite permit its sepn. from cassiterite which remains with it after gravity concn. Scheelite, however, is not magnetic. Scheelite is a minor source of W and is mainly used for Fe-W production, because it is not readily worked up into pure tungstic acid for use in making W powder. Of the various sources of supply, China has lately become most important. For direct Fe-W production only very pure wolframite ore can be used and C must be kept low. W powder (96-98% W) is made by fusion of ores with soda ash, leaching, pptn. with HCl, and reduction by H<sub>2</sub>, hydrocarbon gases or powdered charcoal. Fe-W may be made from a mixt. of scheelite and wolframite in an electric furnace. A satisfactory slag is obtained and a fair yield of metal, but the alloy is high in C. Reduction to Fe-W by Al gives a 95% yield and the app. required is inexpensive. The slag (Al<sub>2</sub>O<sub>3</sub>) is useful as an abrasive. Fe-W containing 80% W is the richest solid alloy which it is possible to produce. Fe-W melts more easily, but W powder is used for the best steel. Direct HCl decomposition of W ores is not satisfactory because incomplete and because the WO<sub>3</sub> so produced contains all the insol. impurities of the ore. Scheelite is not satisfactorily decomposed by soda ash. The reaction is reversible.

JAS. O. HANDY

**Blast furnace built in South Wales.** ANON. *Blast Furnace and Steel Plant 8*, 55-61(1920).—An illustrated description of the furnace and gas-cleaning plant.

R. H.

**New multi-centrifugal gas cleaner.** A. R. SCHULZE. *Blast Furnace and Steel Plant 8*, 553(1920).—An illustrated description of an app. for dry cleaning of blast-furnace gas.

E. H.

**Direct recovery process for flue dust.** GEORGE B. CRAMP. *Blast Furnace and Steel Plant 9*, 198-202(1921).—The installation described consists of a dry dust catcher for receiving and holding heavier particles, followed by a wet gas scrubber for washing out the remaining dust. The dirty wash water is used to wash the wet dust and that recovered in the dry catchers into a settling tank. A thick wet sludge is drawn off at the conical bottom of this tank and is lifted to the top of the blast furnace and there mixed with the stock which goes to make up the charge. Among the advantages gained by this system of recovery are: (1) Immediate sepn. of fine dust from bulkier stock. (2) The same water is used for washing the gas and flushing out the dust catchers. (3) In the settling tank all but 10% of the dust is recovered in wet form, immediately available for charging into the furnace, thus eliminating treatment by briquetting or sintering. (4) Water, power, transportation, labor, and operation costs are less than for any other recovery process. (5) The first cost of a direct recovery plant is substantially less than that for other processes. Also in *Iron Age* 107, 775-8(1921).

S. D. KIRKPATRICK

**The development of flue-dust briquetting.** ALBERT L. STILLMAN. *Blast Furnace and Steel Plant 8*, 395-8(1920).—A review.

E. H.

**New controlling valve for open hearths.** W. H. WHARTON. *Blast Furnace and Steel Plant 9*, 253, 280(1921).—An illustrated description.

E. H.

**Note on the influence of incompletely burned lime in the Thomas process.** ANON. *Rev. Ing.* 28, 79-80(1921).—The  $\text{CaCO}_3$  in the lime used for the dephosphorization decomposes into  $\text{CaO}$  and  $\text{CO}_2$  and lowers the temp. of the charge. The O of the  $\text{CO}_2$  combines with the Mn, which thus no longer prevents the oxidation of the Fe. This results in a lessened yield, which is still further reduced by the action of the S and by mechanical losses due to the evolution of  $\text{CO}_2$  and the cooling of the charge. A. P.-C.

**Smelting (copper) with bituminous coal in blast furnaces.** H. C. ROBSON. *Mining Sci. Press* 121, 400-12(1920).—For 13 yrs. all the blast-furnaces at the Spassky Cu mine in Siberia have been operated with coal for smelting high-grade ore. Three brick blast-furnaces were erected in 1907; inside length of hearth 19.5 ft.; inside width 4 ft.; height of tuyères above hearth, 18 in.; height of feed door above tuyères, 11 ft. There were 32 tuyères, 16 on each side, having an internal diam. of  $2\frac{1}{4}$  in. A drawing of the furnace is shown. The hearth is made from red brick with tamped brasque lining, and the fire walls from unburned quartz brick 12 in. thick. The charge, ore and limestone, is bedded, and all return-slugs are fed separately. The slag and mat run continuously through an open breast into cast-Fe settlers, lined with brick on the back side where the slag enters and protected with coal-ash elsewhere. The ore originally smelted assayed around 20% Cu, the predominating Cu mineral being bornite containing 64% Cu, 24% S, 12% Fe. In later years the % of S increased. The slag produced was more like that from an Fe blast furnace than from a Cu blast furnace. At least 33% of the flux used was necessitated by the shale present in the coal. The coal used amounted to 35 to 40% of the furnace charge. After 9-16 months, the furnace must be shut down owing to accretions on the hearth and the frail nature of the fire walls. The usual amt. of charge smelted per day was only about 80 long tons. A varying % of ironstone used in the charge, to replace a part of the limestone, tended to make a free-running slag and reduce fuel consumption. The best furnace conditions were not

realized until 1917. After the blast pressure was increased from 8-12 oz. to 24 oz. per sq. in., causing a slightly oxidizing atm. to exist in the smelting zone instead of the former highly reducing one, as much as 4.5 tons of charge were smelted per sq. ft. of hearth in 24 hrs., with fuel at 17-20% of the charge. A dense yellow fume of unconsumed hydrocarbons was emitted from the top of the furnace. The use of bituminous coal in the mat-smelting of sulfide Cu ores would ultimately result in marked economy over the use of coke if suitably designed equipment were used. The gas issuing from a furnace running on coal, with a cold top, is easily ignited and burns with a hot flame. The use of coal without waste-heat boilers would probably be cheaper than the use of coke, but, owing to the explosive nature of the gases, the dust could not be caught unless the gases were first burned. Without dust-catching appliances metal losses would be high and would probably more than offset any gain.

A. L. FIELD

**Judging sands for foundry use.** I. HENRY B. HANLEY AND HERBERT R. SIMONDS. *Foundry* 48, 741-6(1920).—Foundry sands may be classified broadly as follows: (1) Molding sand; (2) core sand; (3) racing sand; (4) fire sand; (5) gravel; (6) high-SiO<sub>2</sub> steel molding sand; and (7) parting sand. (1) is usually a mixt. of quartz, feldspar, and clay, having peculiar properties or 'holding a bond when "tempered" with a small amt. of H<sub>2</sub>O. The term often covers (3) also, the difference in the two being merely one of refinement in the bond property. When refinement of finish is necessary, a specially fine-grained sand is necessary. (2) usually is a straight SiO<sub>2</sub> sand, sometimes carrying 10-35% feldspar. Cohesion is obtained by an organic binder, such as linseed oil, molasses, dextrin, resin, etc., or a pitch compd. (4) is usually a coarse SiO<sub>2</sub> sand, with only small quantities if any of clay or feldspar. In the foundry it is mixed with fire-clay to make cupola and ladle linings. (5) is a coarse SiO<sub>2</sub> sand combined with clay to make possible its use as a molding sand. Its function is to increase the porosity of a mold. As castings approach the ton size, porosity of the sand in the mold becomes of great importance. (6) is pure quartz and runs from coarse to fine grades. It must be very infusible and is always artificially bonded. (7) is a pulverized fine quartz sand usually of a fineness to pass a 100-mesh sieve. A table is given showing chem. analyses of the different typical sands, and another table shows the results of sieve tests. Analytical methods for detg. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O, and K<sub>2</sub>O are given. The refractoriness conferred by the SiO<sub>2</sub> in a sand depends upon whether it is present as such or as a constituent of feldspar. The Fe<sub>2</sub>O<sub>3</sub> content often gives a good indication of the amt. of bond in the sand; it may run from 3.5 to 15% in a molding sand. A chem. analysis does not in any way indicate the phys. properties of a molding sand and, since these properties are the most important, chem. analysis should be supplemented by a mechanical analysis where possible. It commonly consists of a sieve test. In addition, a so-called rational analysis is made to obtain information on the relative amts. of the principal mineral constituents—quartz, feldspar, and clay substance. Sands high in feldspar fuse more readily than those of low content. The quartz content of a good refractory molding sand does not run below 90%. The method of detg. clay substance is one of soln. of sol. material in reagents, and not only the hydrated Al silicate (clay) but other sol. silicates are reported as clay substance. Hence this detn. must be used with care. The method is as follows: 1 g. of dry, finely ground molding sand is weighed into a 150-cc. beaker and 15 cc. concd. H<sub>2</sub>SO<sub>4</sub> are added. The mixt. is stirred well and allowed to digest for 12 hrs. at a temp. high enough to give off acid fumes. The soln. is cooled, dild. with 100 cc. of 10% NaOH soln., filtered through a Gooch crucible and washed with about 50 cc. of 25% HCl. The residue is washed with hot H<sub>2</sub>O until free from chloride; it consists of the quartz and feldspar. It is ignited to const. wt. and the clay substance assumed to be equal to the wt. loss over the original sample. The residue is then subjected to an alk. fusion (5 parts of Na<sub>2</sub>CO<sub>3</sub>) and the SiO<sub>2</sub> removed in the usual

way. The filtrate is neutralized with  $\text{NH}_4\text{OH}$ , boiled for a few moments, and filtered. The ppt. is washed with hot  $\text{H}_2\text{O}$  containing a few drops of  $\text{NH}_4\text{OH}$ , then dried and ignited. It is taken as the  $\text{Al}_2\text{O}_3$  content of the sample. It is calcd. to feldspar by assuming the latter to contain 18.34%  $\text{Al}_2\text{O}_3$ . The amt. of quartz is closely indicated by the difference between the feldspar and the clay, detd. as described above. A more reliable method of detg. the bond is known as the bond absorption test. It consists in detg. the amt. of dye absorbed by the colloidal matter present. The amt. of colloidal matter divided by the surface area of the sand gives the bond "density," which furnishes a much more reliable guide to relative bond strength than any other single quantity. An additional point to consider irrespective of surface area is grain shape and amt. of voids. The effect of this factor can be detd. to some extent by experience, although the sieve-test data may be used to obtain approx. results. Evenly graduated amts. remaining on the different sieves indicates a low void. The bond absorption test is carried out as follows: 25 g. of the prepd. molding sand are placed in a 500 cc. wide-mouth bottle, and 250 cc. of distd.  $\text{H}_2\text{O}$  are added, together with 5 cc. of 10%  $\text{NH}_4\text{OH}$ . The bottle is sealed with a glass stopper and paraffin wax and rotated for 1 hr. Then 140 cc. of  $\text{H}_2\text{O}$  are added and the soln. is acidified with about 5 cc. of 10% acetic acid. Sufficient dye (crystal violet) is then added to insure a slight excess after complete absorption. The bottle is again sealed and agitated for 2 hrs. The bottle is removed from the machine and allowed to stand for a few hrs. until the coarser particles have settled to the bottom. From the top portion of the liquid 100 cc. are withdrawn and to this portion are added 25 cc. of  $\text{H}_2\text{O}$  and 2 cc. of 10% acetic acid. A 5-g. skein of mordanted cotton yarn is introduced into the liquid and the temp. gradually raised through a period of 40 mins. to  $60^\circ$ , by which time, through careful movement of the skein, all the dye should be removed from the soln. The skein is removed, washed, and dried at  $75^\circ$  and comparison of its color made against a standard set of skeins, the amt. of dye which was not absorbed by the colloidal matter being this detd. Usually the standard skeins are made by depositing on each of 6 skeins 6, 8, 10, 12, 14 and 16 mg. of crystal violet dye. As a further indication of the bonding value of sands, a transverse strength test is often made. To make this test, 400 g. of molding sand are "tempered" with  $\text{H}_2\text{O}$  up to the point of satn. It is then rammed into a cement briquet mold, having a  $1 \times 1$  in. cross-section at the center. After removal from the mold the specimen is dried overnight and then held for 3 hrs. at  $100^\circ$  in an oven. It is tested in a suitable transverse testing machine, with a breaking capacity of from 1 to 150 lbs. per sq. in. A simple easily constructed machine is described. Photographs of 8 typical sands (8 magnifications) are shown.

A. L. FEILD

**The cause and control of lead poisoning.** WILBER S. SLEMMONS. *Mining Sci. Press* 122, 427-8(1921).—Physiol. action is described. An app. is shown for testing the amt. of Pb in the air of industrial plants. Individuals may develop acute plumbism when working in air containing 0.1 mg. of Pb per cu. ft. A preventive is a proper ventilating system.

A. H. HELLER

**Macroscopic examination of metals.** HENRY S. RAWDON. *Chem. Met. Eng.* 24, 385-7(1921).—The various features revealed by the macroscopic examn. of metals may be summarized under the following types: (1) Chem. non-homogeneity, due to segregation, decarburization, liquation, cementation and similar causes. In wrought metals, lack of complete chem. homogeneity often serves the useful purpose of furnishing a record of the plastic flow of the metal during the various mfg. operations. This is generally revealed by etching. (2) Cryst. heterogeneity due to rate of cooling and to local variations in the cooling. Local overheating may also contribute to this. Etching with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  is admirable for both steel and Cu alloys. (3) Mechanical non-uniformity; presence of internal stresses. When the condition is very severe it may be



revealed by deep etching with Hg solns. for Cu alloys and concd. acids for steels. (4) Physical unsoundness, blowholes, porosity, "flakes," internal discontinuities, etc. X-ray and magnetic examn. in addition to visual examn. may be used to show such features. The general methods of using reagents and S-printing are considered.

V. O. HOMERBERG

**Ferric sulfate as a new etching reagent in the metallography of aluminium.** ROBERT J. ANDERSON. *Metal Ind.* 19, 69-70(1921).—Aq. solns. of  $\text{Fe}_2(\text{SO}_4)_3$  of varying concns. are very satisfactory as etching reagents for distinguishing  $\text{CuAl}$  from  $\text{FeAl}$ , particularly in Fe-bearing light Al-Cu alloys. A 10% soln. is suitable for general use. With this strength of soln., an immersion period of 45 sec. yields good results, and with a 5% soln. an immersion period of about 2 to 5 min. may be employed, 3 min. yielding good results. The microsection must be free from oil or grease. No rubbing of the surface with the reagent is required. The  $\text{CuAl}$  is colored brown to black, while the  $\text{FeAl}$  is practically unaffected. Photomicrographs are given to show the excellent results that are obtainable.

V. O. HOMERBERG

**Finishing metallurgical specimens.** J. F. ADAMS. *Foundry* 49, 117-8(1921).—A treatment is given for the prepn. of specimens for etching.

V. O. HOMERBERG

**Experiments on cupola malleable.** F. H. HURREN. *Foundry* 49, 135-8(1921).—The many points of difference in handling cupola melted metal when compared with the air furnace product are set forth. Details of the annealing procedure are given.

V. O. HOMERBERG

**Steel rails.** C. W. GENNETT, JR. *J. Western Soc. Eng.* 26, Tech. Sec. 77-85 (1921).—G. criticizes the present rail specifications. A number of questions pertinent of modern practice and especially appropriate for original research and study are suggested.

V. O. HOMERBERG

**Iron-nickel alloys.** PAUL D. MERICA. *Chem. Met. Eng.* 24, 375-8(1921).—The principal effects of the addition of Ni to steel are fully treated. The most common grades of Ni steel in com. use together with their properties and uses are considered. The remarkable thermal and elec. characteristics of the high-Ni-Fe alloys are discussed.

V. O. HOMERBERG

**Static and dynamic tension tests on nickel steel.** J. J. THOMAS AND J. H. NEAD. *Trans. Am. Inst. Mining Met. Eng.* No. 1050, 13 pp.(1921).—The expts. described were for the purpose of answering the following questions: Is the total work of rupture more or less for hard steel than for soft steel? How is the total work of rupture affected by the speed of testing, that is, by the rate of application of load? Is the modulus of elasticity const. for all steels? Does ductility have any effect whatever below the elastic limit in the dynamic test? Five pieces of Ni steel, 0.505 in. in diam. and 10 in. gage length, containing 0.42% C, 0.48% Mn, 0.09% Si, 0.035% S, 0.035% P, and 3.20% Ni were prepared as follows: One piece was annealed, 1 was oil-hardened, and 3 were hardened and drawn to different degrees. These test pieces were then tested slowly in tension. Five similar pieces were also tested in an impact machine. A description and the method of operation of this impact machine are given. It was found that the total work of rupture is very low for hard steels under either a slowly or a rapidly applied load. The modulus increases slightly with the higher drawing temps. If the applied stresses would never exceed the elastic limit, and the steel would never be subjected to a live load, a hard steel, and with a smaller area, could be used to obtain the resisting force of a soft steel, owing to the higher elastic limit. Hard steels require little work for rupture and any small suddenly applied load would be sufficient to cause fracture. The ductility and the work of rupture are very low for the low drawing temps. As the ductility increases, the work of rupture increases. For hard steels, therefore, a small load, less than the elastic limit, if applied with sufficient velocity, will develop enough

kinetic energy to cause rupture. It was found that force alone is not the proper criterion by which to measure the strength of material. The work unit is more valuable as a measure of strength, and as ductility is an indication of the work required to rupture, a high ductility should be specified for all parts subject to shock. It was found that steel is in its best condition when quenched and drawn just under its critical temp. The results of work on the test bars are given.

V. O. HOMERBERG

Heat treating plant at Nash Motor Works. ANON. *Iron Age* 107, 895-8(1921).—An illustrated description of a plant for heat-treating roller bearings. E. H.

Notes on heat treatment. L. GREENET. P. DEJEAN. Univ. de Grenoble. *Technique moderne* 13, 104-11(1921).—A summing up of discussions in two previous articles (cf. C. A. 14, 2609; 15, 662) showing points of agreement and disagreement.

A. P.-C.

Irregularity in the coefficient of expansion of gold-copper alloys. ALBERT PORTEVIN AND JEAN DURAND. *Compt. rend.* 172, 325-7(1921).—In an alloy containing 18% Au an irregularity in expansion occurs about 400° on heating and 350° on cooling. The exact behavior depends on the temper.

E. D. WILLIAMSON

Cobalt brasses. LEON GUILLET. *Chem. Met. Eng.* 24, 439-43(1921).—Co enters into solid soln. in one or both of the normal constituents of the Cu:Zn alloys and creates a fictitious compn. which is greater than the real compn. The coeff. of equivalence of Co varies between wide limits, from -0.1 to -1.5, whereas that of Ni is approx. -1.3. A special constituent is isolated as the Co content increases, and the more readily for brasses of lower Cu content. Only traces of this constituent were noted in the samples studied, so that it can be said that the alloy is not thereby altered extensively. It is to be noted, however, that the alloy 60 Cu: 4.8 Co has a considerably decreased elongation and resiliency. Cu:Co solns. are much less extensive than those of Cu:Ni. Additions of Co are not of great industrial importance in the manuf. of brasses. The role of Co approaches that of Ni in brasses, although these 2 metals have completely different effects in steel.

V. O. HOMERBERG

Some properties of white metal bearing alloys at elevated temperatures. JOHN R. FREEMAN AND R. W. WOODWARD. *Metal Ind.* 19, 68(1921).—An app. is described for detg. the yield point and ultimate strength of white bearing alloys at temps. up to 100°. A new design of heating app. is also described for detg. the Brinell hardness of metals at temps. up to 100°. Tests were made on 5 alloys which varied in the relative amts. of Cu, Sb, Sn, and Pb. Tables are given to show the results of the compression tests of the 5 alloys at the various temps. The results of the detns. of Brinell hardness at elevated temps. are also given. The results indicate that the Sn base alloys maintain their properties better at elevated temps. than the alloys contg. Pb. Other tests show that the yield point of Sn base alloys is not affected by heating for 6 weeks at about 180° but the yield point is lowered in the Pb base alloy by heating for 2 weeks at the same temp. Expts. were also made which indicate that up to 5% Pb in a high Sn babbitt does not affect the yield point or ultimate strength at 25° or 75°.

V. O. H.

Anti-friction bearing metals. P. W. PRIESTLEY. *Metal Ind.* 19, 66-7(1921).—A chem., physical, and thermal review is given of anti-friction bearing metals. P. also gives his experience with these alloys in connection with aircraft and automobile construction.

V. O. HOMERBERG

Fifth report to the Corrosion Research Committee. S. H. DUNLOP. *J. Inst. Metals* 24, 372-3(1920).—In connection with the corrosion of condenser tubes, D. considers the effect of the presence of seaweed on the tube plates, and the protection given by cast Fe doors. Corrosion was observed to take place in 2 forms in the case of a turbine destroyer: (1) Of the ferrules and tube ends only, opposite the main inlets, leaving a soft red deposit, and (2) of the top rows of tubes along their whole length, the prod-

uct in this case being a greenish substance. The rapid corrosion was due to the direct contact of the tubes with the seaweed and to the choking of the tube ends and allowing the temp. of the  $H_2O$  in them to rise. In the case of the tubes in a battle cruiser there was not a single case of perforation owing to the time spent in the Firth of Forth, where trouble with weeds was not experienced. Freedom from corrosion in this case was also believed to be due to the fact that the condensers were fitted with cast-Fe doors and these had always been kept uncemented. Also a large number of steel protection plates was fitted in the main inlet pipes, and the temp. of the circulating  $H_2O$  discharge was never allowed to rise above  $80^\circ F.$  under any circumstances. V. O. HOMERBERG

Fifth report to the Corrosion Research Committee. G. D. BENGOUGH. *J. Inst. Metals* 24, 373-5(1920); cf. *C. A.* 14, 1957.—B. disagrees with Dunlop (preceding abstr.) as to the protection given by cast-Fe doors fitted to condensers. It had been definitely proved by observation that the cast-Fe ends of a condenser might become disintegrated in such a way that lumps of material consisting of  $Fe(OH)_2$ , graphite, and apparently Fe became loosened and carried into the tube. The remedy was to paint or cement the  $H_2O$ -ends. B. takes the position that unpainted  $H_2O$ -ends and steel blocks alike were useless except for troubles near the inlet. For such troubles it was best to use steel blocks bolted to the tube plates. V. O. HOMERBERG

Testing electric welds. S. W. MILLER. *J. Electricity* 45, 534(1920); cf. *C. A.* 14, 525. C. G. F.

Chemical methods of de-aeration of water or solutions (corrosion) (WHITE) 14.  
Radiology applied to the testing of materials (FLEMING, CLARK) 3.

Terpin hydrate in mineral flotation. C. L. PERKINS and R. E. SAYRE. U. S. 1,370,357, Mar. 1. Mineral pulp, e. g., Utah Cu ore, is treated with terpin hydrate in the proportion of 2 oz. or more per ton preliminary to flotation sepn., in order to improve the sepn.

Mineral flotation. R. E. SAYRE. U. S. 1,370,366, Mar. 1. A small amt. of a dihydric alc. such as pinacone is added to ore pulps, e. g., Utah Cu ore, preliminary to flotation sepn., in order to facilitate sepn. U. S. 1,370,367 relates to the similar use of the reaction product of  $H_2S$  on acetaldehyde or other thioaldehyde compd. to facilitate flotation sepn.

Briquetting ores. L. A. E. IRAZUSTA. Brit. 155,522, June 29, 1920. A process for conglomerating mineral ores in a pulverulent condition consists in adding a binding agent of pure  $Al_2O_3$  and  $H_2O$  to the ore and forming the mixt. into briquets and then calcining them to form a solid and hard body.

Shaft furnace for treating ores. J. LABARTHE. U. S. 1,370,215, Mar. 1.

Zinc manufacture. R. SIFFERT. Brit. 155,572, Nov. 12, 1920. With a view to increasing the yield of Zn dust obtainable in the manuf. of Zn, a connecting piece having a narrow passage is inserted between the muffle and the collecting chamber for the Zn dust. The chamber is made of correspondingly larger size, and its outlet may be throttled.

Tungsten. C. J. HEAD. Brit. 155,600, Oct. 13, 1917. W powder is obtained from Na or K tungstate or both, e. g., the tungstate obtained as described in 136,577 (*C. A.* 14, 1193) by mixing the tungstate with a chloride, preferably  $NH_4Cl$ , and a reducing agent such as wood, charcoal, anthracite, or sawdust, and heating the mixt. in the form of briquets or otherwise to  $1000-1150^\circ$  for about 15 hrs. The product is either cooled out of contact with air or is quenched in  $H_2O$ . Any sol. tungstates formed may be pptd. with  $CaO$  and  $CaCl_2$  and the Ca tungstate added to a subsequent charge. A suitable construction is specified.

**High-speed steel.** C. M. JOHNSON. U. S. 1,370,020, Mar. 1. A high-speed steel is prepd. containing C 0.20–0.75%, Si 0.35–0.80%, Mn 0.35–0.55%, W 12–18%, Cr 3–5%, V 1.10–1.50% and Mo 0.25–1.00%.

**Cementation.** E. H. JONES. Brit. 134,864, Aug. 12, 1918. Machined articles of soft Fe and mild steel are coated with a metal such as Ni or Co and then subjected to a high temp., *e. g.*, 1000–1200°, while protected from oxidation by a deposit or by a packing until the Ni, etc., is absorbed by the Fe or steel. Cr and V may also be used as the coating-metal if the deposit thereof be protected by a deposit of Fe or Ni. The packing-material may be inert to the metal, or may act as a carburizer.

**Soldering or coating metals.** J. E. RAWORTH. Brit. 156,019, Feb. 24, 1920. In a process of soldering, tinning, or coating Al or Al alloys, the surfaces of the metals are scratched to remove O and the solder or alloy is applied by a rubber consisting of a pad or roll of steel wool. In carrying out the process, the metal to be coated is heated to the m. p. of the solder or alloy, such as an alloy of Zn, Sn, and Pb, which is then melted on the surface and distributed by the rubber. The rubber may be carried by a handle or may be mounted in a machine and rotated or oscillated. In coating an Al surface, after it has been tinned in the above-described manner, it is immersed in molten Sn and then buffed to a higher polish after which it is electroplated. The machine-driven rubber may also be used in filling holes in Al castings. Lengths of Al wire may be joined by this process, thus rendering Al wire suitable for telegraph, telephone, and other elec. purposes.

**Alloys.** A. E. ALEXANDER. Brit., 155,739, Apr. 6, 1920. In making alloys of W with other metals, particularly Fe and steel, the W is used in the form of self-sustaining compressed masses of W powder in tablet or other form. The masses may be added to a molten bath of the other metal or may be added to the other metal prior to melting.

**Alloys.** METALLBANK UND METALLURGISCHE GES. Brit. 155,805, Sept. 17, 1920. Alloys are made by the interaction of one of the metals of the required alloy and an intermediary alloy consisting of another of the metals of the required alloy and another metal. *E. g.*, alloys of Al with Ba, Ca, Sr, Li, Mg, or Be, may be made by the action of Al on an alloy of Pb or Cd or Bi with Ba, etc. The operation may be repeated several times in order to transfer the desired proportion of Ba, etc., into the Al, etc. The production of alloys containing Zn by the method is referred to.

**Copper alloy.** T. KOSUGI. U. S. 1,369,818, Mar. 1. An alloy adapted for propellers or machine parts is formed of Cu 75–90, Al 7–12, Ni 2–7 and Fe 1–6 parts.

**Reducing metallic oxides.** C. M. JOHNSON. U. S. 1,370,021, Mar. 1. Oxides of U, Zr, V, W, Fe, Cr or Mo are reduced by smelting them with both ferro-Si and ferro-Cr, in order to form alloys for high speed steels.

## 10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER

**Formation and autoxidation of coumaranones.** K. v. AUWERS. Marburg. *Ber.* 53B, 2271–85(1920); cf. C. A. 13, 1592.—In earlier papers it has been shown that the formation and rupturing of the O ring of coumaranones are influenced according to definite laws by the number and position of substituents in the two rings and that in compds. of the type  $C_6H_4.CO.CHR.O$  there is a special tendency for the 5-membered

ring to open, for not only is it easily ruptured by ketone reagents such as  $H_2NCONHNH_2$  and  $P-O_2NC_6H_4NHNH_2$  but in some cases the ring spontaneously opens, as the result of more or less rapid autoxidation, with formation of acid esters of *o*-hydroxybenzoic

acids. In all such cases thus far investigated, R has regularly been an alkyl group and it seemed of interest to det. the influence of an aromatic residue. As the result of his work, v. A. finds that Ph hinders the formation of the coumaranone ring far more powerfully than the simpler alkyls and correspondingly decreases the stability of the ring once formed.  $\text{PhCH}_2\text{COCl}$ ,  $b_p$  96°, is obtained in 60-g. yield from 70 g. of the acid heated on the  $\text{H}_2\text{O}$  bath with 3 parts  $\text{SOCl}_2$  until the evolution of  $\text{HCl}$  ceases; 54 g. and 45 g.  $p\text{-MeC}_6\text{H}_4\text{OMe}$  in 113 cc. cold  $\text{CS}_2$  are slowly treated with 54 g.  $\text{AlCl}_3$ , heated 5 hrs. under a reflux on the  $\text{H}_2\text{O}$  bath, freed from the  $\text{CS}_2$  by distn., again treated with 54 g.  $\text{AlCl}_3$ , heated 5 hrs. at 120–30° and decompd. with ice and  $\text{HCl}$ ; the somewhat resinous solid is rubbed with cold  $\text{MeOH}$  and crystd. once from  $\text{MeOH}$ , giving *2-hydroxy-5-methyldeoxybenzoin* (A) in sufficiently pure state (m. 63°) for further work. If the crude product is too tarry, it is taken up in  $\text{Et}_2\text{O}$ , dried with  $\text{Na}_2\text{SO}_4$  and fractionated *in vacuo*; the A,  $b_{11-14}$  210–3°, is a thick, yellow oil immediately solidifying (yield 40–5 g.); it is obtained pure in needles, m. 65°, by repeated crystn. from  $\text{MeOH}$  or benzene, dissolves in alkalis with deep yellow color and gives a violet color with  $\text{FeCl}_3$ ; *acetate* (30–5 g. from 45 g. A boiled with an equal wt. of  $\text{AcCl}$  until the evolution of  $\text{HCl}$  ceases (about 3 hrs.), cooled and poured into dil. soda), needles from alc., rhomb-shaped crystals from benzene, m. 73–4°. The desired 2-phenyl-5-methylcoumaranone (B) not having been formed in the above reaction, 6 g. of the above acetate in 20 cc. of  $\text{CS}_2$  was treated dropwise with 3.6 g.  $\text{Br}$  in 4 cc.  $\text{CS}_2$ , giving the *acetate*, silky needles, m. 118–9°, of  *$\alpha$ -bromo-2-hydroxy-5-methyldeoxybenzoin* (C) (0.8 g. from 2 g. of the acetate in 6–7 cc.  $\text{AcOH}$  boiled 10 min. with 2 cc. of  $\text{HBr}$  satd. at 0°), faintly yellowish quadratic leaflets from  $\text{MeOH}$  or benzene, m. 106°, very sensitive to moisture. When C is dissolved in cold  $\text{NaOH}$ , filtered from the small amt. of oil which usually remains undissolved and acidified, there are pptd. white flocks, probably a mixt. of B and 5,2- $\text{Me}(\text{HO})\text{C}_6\text{H}_3\text{COCH}(\text{OH})\text{Ph}$ , which, after draining, are allowed to stand in the air until the mass, after turning viscous, then oily, has become solid (about 3 weeks for 10–20 g.); this is then sepd. by fractional crystn. from benzene into *O-benzoyl-p-cresotic acid* (D) (1 part), silvery, felted needles, m. 155–6°, and *2-hydroxy-5-methylbenzil* (E) (3–4 parts), yellowish prisms, m. 90–1°, gives a dirty violet color with  $\text{FeCl}_3$ , easily sol. in dil. alkalis with yellow color, hardly sol. in soda, unchanged by boiling 5 hrs. in a little alc. with 10%  $\text{H}_2\text{SO}_4$  but if the original product of the action of  $\text{NaOH}$  on C is heated with  $\text{H}_2\text{SO}_4$  there is formed a mixt. of  $\text{BzOH}$  and  $\text{Me}(\text{HO})\text{C}_6\text{H}_3\text{CO}_2\text{H}$ . *Disemicarbazone* of E, needles, m. 193–4°; *p,p'-dinilroosazone*, dark red finely cryst. powder, turns yellow 225–40°, m. 280–2°, *methyl ester*, prepd. with alk.  $\text{Me}_2\text{SO}_4$ , needles from benzene, m. 106–6.5°, identical with the product obtained by boiling 5,2- $\text{Me}(\text{MeO})\text{C}_6\text{H}_3\text{COC}(\text{NOH})\text{Ph}$  (see below) 4 hrs. with 30–40 parts of 20%  $\text{H}_2\text{SO}_4$ . The behavior of E on methylation, its yellowish color and its reaction with  $\text{FeCl}_3$  prove sufficiently that it is really a benzil deriv. and not a hydroxycoumaranone,  $\text{MeC}_6\text{H}_3\text{COC}(\text{OH})\text{Ph.O}$  (F). The most probable explanation of the action of alkali

on C is that the greater part of it is converted into the benzoin,  $\text{Me}(\text{HO})\text{C}_6\text{H}_3\text{CH}(\text{OH})\text{Ph}$ , which is oxidized to E, while a smaller part goes over, by loss of  $\text{HBr}$ , into B, which, possibly through F, is converted into D; the assumption that F is an intermediate product is not necessary, however, as D may be formed directly from B by the addition of a mol. of  $\text{O}_2$  to its enol form. Attempts to prep. B from C by means of  $\text{NaOAc}$  likewise failed; different products were obtained in different expts. for reasons which could not be discovered. Thus, from 2 g. C and 1 g.  $\text{NaOAc}$  boiled about 10 min. in aq. alc. were obtained a high melting substance (see below), D and other products; similar results were obtained with 1 g. C and 2 g.  $\text{NaOAc}$  allowed to stand overnight; when the components were boiled 45 min. a small amt. of a substance m. 64–5°, crys-

tals from benzine, resulted; in an attempt to prep. more of the last compd. there was obtained a compd. m. 227–32°, crystals from AcOH, having the compn. of a phenyl-methylcoumaranone but apparently of double the mol. wt. Again, when it was attempted to prep. B by boiling C 5 hrs. with 5 parts PhNEt<sub>3</sub>, the product was A; *semi-carbazone*, somewhat greenish crystals, m. 204–5°; *p*-nitrophenylhydrazone, orange-yellow needles, m. 203–4°. The *methyl ether* of A was several times obtained in good yield when *p*-MeC<sub>6</sub>H<sub>4</sub>OMe, PhCH<sub>2</sub>COCl and AlCl<sub>3</sub> were condensed as described above except that the product was not treated a second time with AlCl<sub>3</sub> after distg. off the CS<sub>2</sub>; by this process, however, the ether is more or less hydrolyzed and for the re-conversion of the product into the ether the alk. Me<sub>2</sub>SO, process is not well adapted as the Na salt of the A is difficultly sol. in 8% NaOH and on the other hand has a great tendency to hydrolyze so that the A can be dissolved only in a great excess of very dil. NaOH. Recourse was, therefore, had to MeI: 4.08 g. Na in 32 g. MeOH, 40 g. A in concd. MeOH soln. and 50 g. MeI were boiled to decolorization under a Hg seal, freed from the alc. by distn., poured into H<sub>2</sub>O, taken up in Et<sub>2</sub>O and dried; the ether, b<sub>14</sub> 205–7°, is a faintly yellow oil slowly depositing prismatic crystals m. 75°; *β*-oxime (0.7–1.65 g. from 5 g. of the ether in 2–3 parts AcOH treated with a few drops AmNO<sub>2</sub> and 1–2 cc. concd. HCl, then dropwise with 2.7 g. AmNO<sub>2</sub>, allowed to stand 12 hrs., dild. with Et<sub>2</sub>O, shaken out with NaOH and pptd. with AcOH), needles from C<sub>6</sub>H<sub>6</sub>, m. 143–4°; *dioxime* (0.1 g. from 1 g. of the mono-oxime in alc. boiled 9 hrs. with 0.52 g. NH<sub>2</sub>OH.HCl), silky, felted needles from MeOH or EtOH, m. 225–7°. When the mono-oxime was boiled with NH<sub>2</sub>CONHNH<sub>2</sub>.HCl and NaOAc, there was no reaction after 5 days.

CHAS. A. ROUILLER

### 3-Hydroxythionaphthenes. K. v. AUWERS. Marburg. Ber. 53B, 2285–99(1920).

—As most of the 3-hydroxythionaphthenes are easily sol. in aq. alkalies and in such solns. can be converted, like phenols, into ethers, esters and azo dyes they have generally been formulated as HO derivs. of thionaphthene. In support of this view is the fact, apparently thus far not recorded, that they form Ac derivs. when heated with AcCl or Ac<sub>2</sub>O. On the other hand they combine in the ketone form with aldehydes and react in the normal way with typical ketone reagents. In order to det. whether, in homogeneous state, they are enols or ketones, some of them were titrated with Br, both by the direct and the indirect methods. Very exact values could not be obtained as most of these compds. are but little sol. in alc. at –10° and either very dil. solns. must be used or the measurements must be made at higher temps., which increases the danger of rearrangement. Moreover, owing to the tendency of these compds. to form dyes, most of their solns. are colored and thus obscure the end-point. Again, the values obtained vary somewhat according as the Br is added more or less slowly. In almost all cases, however, the amt. of Br consumed corresponded to only 1–5% enol. Accordingly it is probable that the "hydroxythionaphthenes" in the solid state, like the coumaranones and hydrindones, are true ketones and should, therefore, more properly be designated as thiocoumaranones or thionaphthanones. From a study of a number of these compds. v. A. finds that they resemble the coumaranones in that they can easily react as enols both in the free state and in alk. soln. while the hydrindones do not; on the other hand they resemble the hydrindones and differ from the coumaranones in that their 5-membered ring apparently cannot be ruptured by ketone reagents. This has been shown with certainty for those representatives of these compds. which have no substituents on the S ring; for those with alkyl substituents on this ring this statement is at present only probable and must be further tested. Common to all three classes of compds. is the autocondensation of those representatives having free CH<sub>3</sub> groups next to the CO, with formation of compds. of the type  $\text{X.R.CO.C=}$ ;

(X = O, CH<sub>3</sub> or S). In their behavior on autoxidation, however, hydroxythionaphthenes substituted in position 2 stand alone, judging from the reaction of 2-phenyl-3-hydroxythionaphthene, which gives the compd.  $\text{[S.R.CO.CPh-]}_2$ , 3-Acetoxythio-

naphthene, from the hydroxythionaphthene (A) boiled with 4 parts AcCl until the evolution of HCl ceases (3-4 hrs.), light yellow oil,  $b_{15}$  165°,  $d_{20}^{20}$  1.2580,  $n_D^{20}$  1.57918, 1.60464, 1.62328 for  $\alpha$ , D and  $\beta$  at 20.4°, soon becomes dark red and begins after a time to change into a solid, probably an oxidation product; this was accidentally obtained in larger amt. when 25 g. o-HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>OH and 50 g. Ac<sub>2</sub>O which had been boiled 1 hr. were allowed to stand 40 hrs.; there resulted a thick cryst. magma which, recrystd. from MeOH or EtOH, yielded long, faintly reddish yellow needles, m. 164-5°, of the compn. C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub>. A treated with somewhat more than 2 mols. NH<sub>2</sub>CONHNH<sub>2</sub>·HCl and NaOAc in aq. alc. gives the semicarbazone as a reddish ppt. (which was allowed to stand 2 days under the fluid), completely insol. in alkalis, forming, after boiling out with alc., pink needles, sinters 220°, m. 224-6°; the same result was obtained after 1 week at 40-50°. *p*-Nitrophenylhydrazone, from A in alc. with a concd. aq. soln. of 1 mol. *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHNH<sub>2</sub>·HCl after 2 days, dark red needles with violet luster, pptd. from alc. by H<sub>2</sub>O as a red-brown powder, m. (after 2 such treatments) 185-90°; by repeated pptn. from alc. with H<sub>2</sub>O was obtained another sample, which was bright red and m. 205°; the product obtained with 2 mols. of the hydrazine after 2 hrs. in alc. on the H<sub>2</sub>O bath and repeatedly boiled out with alc. was a brown-red granular powder, m. 251-6° (the mixt. with the first prepn. m. 212°); in spite of the higher m. p., however, the last compd. is also a monohydrazone. 6-Methyl-3-hydroxythionaphthene, obtained in 60-70% yield from 5,2-Me(HO<sub>2</sub>C)C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH and NaOH (Ger. pat. 204,763), snow-white needles gradually becoming a soft pink, m. 86-7°; acetate, thick golden yellow oil,  $b_{12-4}$  168.5°, becomes reddish brown on long standing and slowly changes into a solid; semicarbazone, pink needles, m. 232-3°, insol. in alkalis; *p*-nitrophenylhydrazone, from the ketone boiled 4 hrs. in alc. with excess of O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHNH<sub>2</sub>·HCl, red-brown granular substance, m. 222-7° (another sample prepd. by heating 10 hrs. m. 245-52° and when it was repeatedly boiled out with alc. the m. p. slowly rose to 272-4°). 6-Bromo-4-methyl-3-hydroxythionaphthene, obtained in 35% yield from 10 g. 5,3-BrMeC<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H gently warmed about 10 min. on the H<sub>2</sub>O bath with 20 g. SOCl<sub>2</sub>, freed from the excess of SOCl<sub>2</sub> with dry air, dild. with 2 vols. CS<sub>2</sub>, slowly treated in the cold with 5.1 g. AlCl<sub>3</sub>, sep'd. from the CS<sub>2</sub>, decompd. with ice and HCl and distd. with steam, long, slender needles from benzene or MeOH containing a little SO<sub>2</sub>, m. 134-5°, slowly turns pink and then red; semicarbazone, obtained in only very small amt. after 15 hrs., is a colorless alkali-insol. substance; the *p*-nitrophenylhydrazone is obtained, after 5 hrs.' boiling, as a yellow-brown powder, m. around 200°, probably contaminated with a dye produced by oxidation. 5-Chloro-3-hydroxythionaphthene (Ger. pat. 224,567), from *p*-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CO<sub>2</sub>H boiled 15 min. with 2 parts Ac<sub>2</sub>O, heated 5 min. with excess of NaOH, acidified and distd. with superheated steam, flesh colored crystals from benzene, m. 100°; semicarbazone, pink powder, m. 253°, insol. in alkalis; *p*-nitrophenylhydrazone, red-brown powder, m. 270°. 5-Chloro-6-ethoxy-3-hydroxythionaphthene, faintly pink needles from alc., m. 135.5-6.5°, obtained by boiling 5 min. with NaOH and a little alc. the acetate, needles from MeOH and EtOH, m. 128-9°, which is prepd. by boiling 4,3-Cl(EtO)C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H 5-6 hrs. with 2-3 parts Ac<sub>2</sub>O; semicarbazone, obtained in small amts. after 17-8 hrs. at 40-50°, dark pink ppt. insol. in NaOH, m. 250°; *p*-nitrophenylhydrazone, dark red to brown cryst. ppt., m. 240-52°.  $\alpha$ -*p*-Thiocresylpropionic acid, from 6 g. *p*-MeC<sub>6</sub>H<sub>4</sub>SH, 6 g. NaOH and 7-8 g. MeCH<sub>2</sub>BrCO<sub>2</sub>H in H<sub>2</sub>O boiled 15 min., crystals from benzene, m. 77.5-8.5°; when condensed with SOCl<sub>2</sub> and AlCl<sub>3</sub> it yields a thick, red oil, which with superheated steam gives a very small amt. of a colorless oil; the distillate is extd. with Et<sub>2</sub>O, the Et<sub>2</sub>O distd. off,

the tarry residue again taken up in  $\text{Et}_2\text{O}$ , freed from any hydroxythionaphthene with  $\text{NaOH}$  and pptd. with  $\text{H}_2\text{SO}_4$  and the ppt. is taken up in  $\text{Et}_2\text{O}$ , dried and again evapd. There is thus obtained a solid yellowish substance, m.  $117^\circ$ , which may have been the desired 2,5-dimethyl-3-hydroxythionaphthene but the amt. was too small for further study. *sym-m-Thioxylene methyl ether*, thick oil,  $b_{74}$   $127^\circ$ , is obtained from the xyleneol with alk.  $\text{Me}_2\text{SO}_4$ ; with 1 mol.  $\text{MeCHBrCOBr}$  in  $\text{CS}_2$  and 1.5 mols.  $\text{AlCl}_3$ , after decompn. with ice and  $\text{HCl}$ , distn. with superheated steam and extn. with  $\text{Et}_2\text{O}$ , is obtained a red, thick oil (2,4,6-trimethyl-3-hydroxythionaphthene?), which, however, yielded no semicarbazone nor nitrophenylhydrazone.  $\alpha$ -[*sym-Bromomethylthiophenyl*]propionic acid, crystals from benzene, m.  $78-9^\circ$ ; with  $\text{SOCl}_2$  and  $\text{AlCl}_3$  it gives a thick, red oil, slowly yielding with superheated steam a colorless oil which at once turns yellow in the receiver; the  $\text{Et}_2\text{O}$  ext. of the distillate gives a resinous mass pptd. from alkalies by acids as a light yellow oil, which at once begins to resinify again. In a second expt. the crude product (without steam distn.) was taken up in  $\text{Et}_2\text{O}$ , freed from hydroxythionaphthene with alkali, pptd. by acids, again dissolved in  $\text{Et}_2\text{O}$  and evapd.; there was thus obtained a brown oil showing less tendency to resinify; this with  $\text{H}_2\text{NCONHNH}_2$  gave a small amt. of a substance, m.  $238-7^\circ$ , insol. in alkalies, and with  $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHNH}_2$  the impure 2,4-dimethyl-6-bromo-3-hydroxythionaphthene *p*-nitrophenylhydrazone as a yellow-brown mass. 2-Phenyl-3-hydroxythionaphthene (Kalb and Bayer, C. A. 8, 707) in alc. with  $\text{H}_2\text{NCONHNH}_2\cdot\text{HCl}$  and  $\text{NaOAc}$  gives after 11 days the oxidation product  $(\text{S}_2\text{C}_6\text{H}_5\text{CO.CPh-})_2$ , m.  $223-4^\circ$  (K. and B.,  $231^\circ$ ); with  $\text{O}_2\text{NC}_6\text{H}_4\text{NHNH}_2$  are obtained

only tarry, low-melting products. 2-*p*-Nitrophenyl-3-hydroxythionaphthene (Apitzsch, C. A. 8, 126) is unchanged by  $\text{H}_2\text{NCONHNH}_2$  after several days and by  $\text{O}_2\text{NC}_6\text{H}_4\text{NHNH}_2$  after 5 hrs. boiling.

CHAS. A. ROULLER

1,5-Dimethyl-1-dichloromethylcyclohexa-3,5-dien-2-one. K. v. AUWERS AND K. ZNÖGLER. Marburg. Ber. 53B, 2299-304(1920); cf. Ber. 35, 4210(1902).—In investigations of the chlorinated hydroaromatic ketones formed from phenols,  $\text{CHCl}_3$ , and alkalies a whole series of *p*-comps. of the type  $\text{Me}(\text{Cl}_2\text{CH})\text{:C}_6\text{H}_4\text{:O}$  were prepd. but only one *o*-deriv., although it was conjectured, but without certainty, that from *asym-m*-xyleneol (A) the *o*-isomer is formed along with the *p*-compd. This has now been shown to be true but the *o*-compd. is formed only as a by-product and as it could be sepd. only by repeated fractionation *in vacuo* and remained oily the yield was small (20-30 g. from 600 g. xyleneol), and it is not wholly certain that it was obtained perfectly pure. That it is really an *o*-compd. is shown by comparison of its physical consts. with those of the *p*-deriv. and of the two simplest corresponding ketones (from *o*- and *p*- $\text{MeC}_6\text{H}_4\text{OH}$ ), and also by its chem. properties. The crude product from A,  $\text{CHCl}_3$  and  $\text{NaOH}$  was not distd. with superheated steam, as before, but *in vacuo*; on cooling and scratching, most of the *p*-compd. sepd. from the distillate and was drained off; the remaining oily portions were then systematically fractionated until a const. low-boiling fraction was obtained which deposited no solid on strong cooling. The 1,5-dimethyl-1-dichloromethylcyclohexa-3,5-dien-2-one is a faintly yellow oil,  $b_{18}$   $125-5.5^\circ$ ,  $b_{18}$   $127.5-8.5^\circ$ ,  $d_{18}^{19.8}$  1.2250,  $n$  1.52906, 1.53366, 1.54766 for  $\alpha$ , D and  $\beta$  at  $19.8^\circ$ ,  $E_Z$  0.75, 0.78, 50% for  $\alpha$ , D and  $\beta$ — $\alpha$ , does not react with  $\text{H}_2\text{NCONHNH}_2$  or  $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHNH}_2$  even after boiling for a day in alc.; an  $\text{Et}_2\text{O}$  soln. added to 2.4 g. Mg and 16 g. MeI in 50 cc.  $\text{Et}_2\text{O}$  at such a rate that the  $\text{Et}_2\text{O}$  kept boiling and then allowed to stand 1 hr. gives 1,4,5-trimethyl-1-dichloromethylcyclo-5-hexen-2-one, oil of a peppermint odor,  $b_{18}$   $125-7^\circ$ ,  $d_{18}^{19.3}$  1.1649,  $n_D^{18.3}$  1.50872; during the distn. a little  $\text{H}_2\text{O}$  is split off, showing that during the Grignard reaction a little tert. alc. is formed (either from the *o*-ketone, or more probably from some admixed *p*-isomer), so that the product is probably not quite pure; if it is slowly added to 10 parts cold  $\text{H}_2\text{SO}_4$  and allowed to stand 2 days it



rearranges into the *cyclo-3-hexen-2-one*, oil of a peppermint odor;  $b_p$  155-8°;  $d_4^{20}$  1.1972,  $n_D^{20}$  1.52013, 1.52392, 1.53417, 1.54298 for  $\alpha$ , D,  $\beta$  and  $\gamma$  at 19.7°;  $E_Z$  0.44, 0.47 30%, 30% for  $\alpha$ , D,  $\beta$ - $\alpha$  and  $\gamma$ - $\alpha$ .  
CHAS. A. ROULLER

**Furethylamine and tetrahydrofurethylamine.** A. WINDAUS AND O. DALMER. Univ. Göttingen. *Ber.* 53B, 2304-8 (1920).—Pharmacological investigations in the series of the phenol bases and aminoalkylimidazoles have shown that more than all others those bases in which the ring and the  $NH_2$  group are sepd. by a chain of two C atoms show a pronounced sympatho-mimetic action, and W. and D. have now synthesized two such bases in the furan series. *Ethyl furopropionate*, from the acid boiled 4 hrs. with 8 parts alc. containing 5% of  $H_2SO_4$ , liquid of a pleasant fruity odor,  $b_p$  209°, gradually becomes yellowish in the air; 12 g. heated 7 hrs. under a reflux with 5 g. of 90%  $NH_4.H_2O$  gives the *hydrazide*,  $m.$  68-72°, which in alc. with excess of  $MeOC_2H_4CHO$  and dil. NaOH forms the *amisalhydrazide*,  $C_6H_5OCH_2CH_2CONHN:CHC_2H_4OMe$ , long needles from alc.,  $m.$  103°. The hydrazide (12 g.) in  $H_2O$  treated at 0° with 60 cc. of 2  $N$   $H_2SO_4$  and then slowly with 6 g.  $NaNO_2$  in  $H_2O$ , quickly extd. twice with  $Et_2O$ , washed with  $H_2O$ , dried with  $CaCl_2$ , dild. with 100 cc. MeOH, cautiously freed from the  $Et_2O$  by distn., boiled 2 hrs. under a reflux and evapd. yields the *urethan* as a thick, yellowish oil, 2 g. of which, mixed with 8 g. CaO and distd. under atm. pressure gives *furethylamine* (A), light yellow liquid,  $b_p$  159°, eagerly absorbs  $CO_2$  from the air with formation of a cryst. *carbaminate*,  $m.$  84°, smoothly formed from A in  $Et_2O$  with dry  $CO_2$ ; *benzoyl derivative*, long needles from dil. alc.,  $m.$  81°; *picrolonate*, yellow-orange platelets and prisms from  $H_2O$ ,  $m.$  204° (decompn.). *Tetrahydrofuropropionic acid*, from furacrylic acid in soda with Pd sponge and  $H_2$ , thick liquid of peculiar odor,  $b_p$  263°; *ethyl ester*, liquid of a faint odor,  $b_{760}$  221°, is converted through the hydrazide, azide and urethan into *tetrahydrofurethylamine* (B), liquid of an intensely basic odor,  $b_{760}$  173°; *carbaminate*,  $m.$  76°; *picrate*, orange-yellow needles from  $H_2O$ ,  $m.$  129°; *picrolonate*, orange-yellow needles from  $H_2O$ ,  $m.$  175°. A (0.0025 g. in a cat) produces an immediate but only short-lived fall in blood pressure without marked influence on the pulse and respiration; it contracts smooth muscle (about 0.25 as powerfully as hydrastinine). B has no effect on the blood pressure (0.005 g.); on the isolated uterus, it is about 0.5 as powerful as hydrastinine.  
CHAS. A. ROULLER

**Pivalylacetic ester.** ERIK WAHLBERG. Akademiska Boktryckeriet, Upsala, *Thesis* 1914, 74 pp.—Parts of this thesis have been previously published in German and abstracted (*C. A.* 5, 3425, 3426). The work reported consisted mainly in the prepn. of a number of related compds., purifying these by repeated crystns., analysis, and  $m.$  p. detns. For the sake of brevity the compds. formed are numbered and here given in a tabular order, omitting such facts as have already been given in *C. A.* In the original almost all the preps. are given 2  $m.$  ps. differing by just 1°; of these only the first is mentioned below. I.  $\omega$ -Bromopinacolin (2,2-dimethyl-4-bromo-3-butanone),  $Me_2CCO-CH_2Br$ . II. Cyanopinacolin. III. *Sodium oxymethylenepinacolin*. To pinacolin and  $HCO_2Et$  in  $Et_2O$  was added a calcd. amt. of Na and an equal wt. of abs.  $EtOH$ . The salt is yellowish red and gives a deep violet color with  $FeCl_3$ ; with  $NH_4OH.HCl$  it forms an oil, which after congealing  $m.$  87° and gives a green color with  $FeCl_3$ . IV.  $\omega$ -Cyanopinacolin cyanohydrin,  $Me_2CC(OH)(CN)CH_2CN$ , obtained by evapg. the  $EtOH$  mother liquors from II. adding  $H_2O$ , extg. with  $Et_2O$  and pptg. the ext. from  $C_6H_6$  with ligroin,  $m.$  80-85°. The same compd.  $m.$  85°, was also prepd. by allowing II to stand in contact with aq. KCN for 2 days. When this compd. was warmed on a water bath CN was driven off and it reverted to II. A part of this prepn. left in the desiccator throughout the summer changed as to  $m. p.$  from 85° to 67°. V. *3-tert-Butyl-5-imino-4,6-dihydroisoxazole*,  $Me_3CC:N.O.C(:NH).CH_3$ , from II in 4 parts glacial AcOH with the calcd.

amt. of  $\text{NH}_4\text{OH}$ ,  $\text{HCl}$  and  $\text{AcONa}$ , thin colorless plates, m.  $98^\circ$ . There was considerable trouble in isolating the crystals. They are very sol. in  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{Et}_2\text{O}$ ,  $\text{PrOH}$ ,  $\text{AmO}$ ,  $\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{Ac}_2\text{O}$ ,  $\text{CHCl}_3$ , and insol. in  $\text{H}_2\text{O}$  and ligroin. When the  $\text{Et}_2\text{O}$  soln. was evapd. there resulted a viscous oil which was sol. in  $\text{HCl}$  and from which it was pptd. by alkalis. VI. Ethyl pivalylimidoacetate hydrochloride,  $\text{Me}_3\text{CCOCH}_2\text{C}(\text{NH}_2\text{HCl})\text{OEt}$ , prepd. by passing dry  $\text{HCl}$  through II in  $\text{Et}_2\text{O}$  and abs.  $\text{EtOH}$  (1 mol. to 1.5 mol. in 5 parts  $\text{Et}_2\text{O}$ ), large well formed prismatic crystals, m.  $129^\circ$ . Yield, 70%. VII. The free imido ester, prepd. from VI with  $\text{NaOH}$ , m.  $58^\circ$ , had a marked odor, is very sol. in  $\text{EtOH}$ ,  $\text{Et}_2\text{O}$ ,  $\text{Ac}_2\text{O}$ , and  $\text{CHCl}_3$ . VIII. Pivalylacetamide. IX. Ethyl pivalylacetate. X. Free acid. XI. Ethyl methylpivalylacetate  $\text{Me}_3\text{CCOCHMeCO}_2\text{Et}$ . XII. Free acid, m.  $101^\circ$ , loses 1 mol.  $\text{CO}_2$  on melting, forming  $\text{Me}_3\text{CCOEt}$ , very sol. in  $\text{EtOH}$ ,  $\text{Et}_2\text{O}$  and warm  $\text{C}_6\text{H}_6$ , only slightly sol. in cold  $\text{C}_6\text{H}_6$  and insol. in ligroin, gives no color reaction with  $\text{FeCl}_3$ . XIII. Ethyl pentamethylacetacetate,  $\text{Me}_3\text{CCOCMe}_2\text{CO}_2\text{Et}$ . XIV. Pinacolylpivalylacetic acid,  $\text{Me}_3\text{CCOCH}(\text{CO}_2\text{H})\text{CH}_2\text{COCMe}_2$ , obtained by allowing I and the Na salt of IX to stand for some time in  $\text{Et}_2\text{O}$  at room temp., then heating on a water bath, sapong. the resulting ester (b.  $155.5^\circ$ ) and extg. with  $\text{Et}_2\text{O}$ , m.  $61^\circ$ . Yield 60%. XV. Pinacolylpinacolin,  $(\text{Me}_3\text{CCOCH}_2)_2$ , obtained when XIV is heated to its m. p. or when its  $\text{Et}_2\text{O}$  soln. is allowed to evap. spontaneously, m.  $25^\circ$ . After distn. under reduced pressure it m.  $22^\circ$ . In a freezing mixt. needle crystals, m.  $19^\circ$ , sep. On melting these crystals there resulted a translucent mass which became a transparent liquid at  $25^\circ$ . Between these two temps. the substance is a cryst. fluid. The molten mass has a rounded segmented dendritic structure. It gives a pyrrole reaction but pyrrole derivs. were not obtained. It is sol. in org. solvents. XVI. 2,2,7,7-Tetra-methyloctane 3,6-dioxime,  $(\text{Me}_3\text{CC}(\text{NOH})\text{CH}_2)_2$ , produced by treating XV with  $\text{NH}_4\text{OH}$ ,  $\text{HCl}$  and  $\text{AcONa}$ , small colorless crystals, m.  $265^\circ$ , sol. in warm glacial  $\text{AcOH}$ , and boiling  $\text{EtOH}$ , but insol. in  $\text{C}_6\text{H}_6$ , ligroin and boiling dil.  $\text{NaOH}$ . XVII. Phenacylpivalylacetic acid,  $\text{Me}_3\text{CCOCH}(\text{CH}_2\text{COPh})\text{CO}_2\text{H}$ , prepd. from the calcd. amt. of  $\text{PhCOCH}_2\text{Br}$  and the Na salt of IX in  $\text{Et}_2\text{O}$  and purified by pptg. from  $\text{C}_6\text{H}_6$  with ligroin, m.  $108.5^\circ$ , sol. in  $\text{EtOH}$ ,  $\text{CHCl}_3$ , glacial  $\text{AcOH}$ , and  $\text{C}_6\text{H}_6$ , but not sol. in ligroin, slightly sol. in water, giving an acid reaction. In melting it gave off 1 mol  $\text{CO}_2$ . XVIII. Pivalylsuccinic acid,  $\text{Me}_3\text{CCOCH}(\text{CH}_2\text{CO}_2\text{H})\text{CO}_2\text{H}$ , prepd. like XIV and XVII, using  $\text{ClCH}_2\text{CO}_2\text{H}$  and heating for 5 days, colorless cryst. mass, m.  $108^\circ$ , easily sol. in  $\text{EtOH}$  and  $\text{Et}_2\text{O}$  but insol. in  $\text{C}_6\text{H}_6$  and ligroin, gives no color reaction with  $\text{FeCl}_3$ , in melting loses 1 mol  $\text{CO}_2$ . The ester first formed b.  $157-60^\circ$ . Yield 70%. XIX. 3,3,3-Tri-methylsuccinic acid,  $\text{Me}_3\text{CCOCH}_2\text{CH}_2\text{CO}_2\text{H}$ , formed from XVIII by loss of 1 mol. of  $\text{CO}_2$ , m.  $68.5-68^\circ$ , very sol. in  $\text{EtOH}$ ,  $\text{Et}_2\text{O}$ ,  $\text{CHCl}_3$ , and  $\text{C}_6\text{H}_6$ , less sol. in cold water and insol. in ligroin. XX. Diethyl dipivalylsuccinate,  $[\text{CH}(\text{COCMe}_3)\text{CO}_2\text{Et}]_2$ . The Na salt of IX in  $\text{Et}_2\text{O}$  was heated with I for 0.5 hr. on the water bath, giving a light yellow oil which would not solidify on cooling; its odor was suggestive of Et methylpivalylacetate, it gave no color reaction with  $\text{FeCl}_3$ , no pyrrole reaction, and was not sol. in warm dil.  $\text{NaOH}$ . Attempts to obtain XV from the mixt. were unsuccessful. After some time crystals sepd. from the oil and after crystn. from  $\text{MeOH}$  m.  $74^\circ$ . The residual oil after crystn. was distd., giving a heavy-flowing liquid from which sepd. crystals readily sol. in  $\text{EtOH}$  (from which they did not recryst.), m.  $99-101^\circ$ . On distg. a second portion more slowly, the crystals obtained m.  $146^\circ$ . Only a small amt. of the material was available for analysis. The analytical data correspond to  $\text{C}_{24}\text{H}_{42}\text{O}_8$  and  $\text{C}_{24}\text{H}_{41}\text{O}_8$ , resp. W. believes that the ester lost 2 mols alc. XXI. Ethyl methylenebis-pivalylacetate. Two mols. of IX in  $\text{Et}_2\text{O}$  was treated with 1.2 mols. 40%  $\text{HCHO}$  and allowed to stand for 1 week, then distd. with  $\text{H}_2\text{O}$  and the resulting oil was washed and dried and then distd. at  $110^\circ$  (15 mm.). The residue was heated at a high temp. and on cooling formed a glassy mass. Inasmuch as the product could be neither distd. nor crystd., the analyses

were not at all satisfactory. W. believes that the material consisted chiefly of **XXI**. With  $\text{FeCl}_3$  it gave a reddish brown color. **XXII**.  $\alpha$ -Pivalylcoumarin,  $\text{C}_6\text{H}_5\text{CH}:\text{C}(\text{COCMe}_3)\text{CO}_2\text{O}$ . Mol. proportions of **IX** and salicylaldehyde and a few drops

of piperidine were set aside for 6 days. The liquid solidified when disturbed, forming a brown mass, sepg. from MeOH in colorless crystals, m.  $89.5-90^\circ$ . Yield, 40%. With NaOH it gave a yellow soln., from which it sepd. very slowly on careful neutralization, and rapidly if the acid was added in excess. When the acid was added to the NaOH soln. until the color disappeared, i. e., just under neutralization, and the soln. extd. with  $\text{Et}_2\text{O}$ , a substance was removed which formed a glassy mass and had a strong acid reaction. This decolorized soln. gave a colorless flocculent ppt. with Ag salts. The Ag compds. from alc. were fine orange ppts. which were unstable in the presence of moisture. The compd. is not very stable. It is destroyed when NaOH is added to its alc. soln., giving as one product an insol. colorless material. It decomps. very rapidly in boiling NaOH. **XXIII**. Ethyl  $\alpha$ -pivalyl-3-nitro-2-hydroxycinnamate,  $\text{Me}_3\text{CCOC}(\text{CO}_2\text{Et})\text{CHC}_6\text{H}_4(\text{OH})\text{NO}_2$ , prepd. by treating **IX** and the calcd. amt. of *o*-nitrosalicylaldehyde in the least necessary amt. of cold  $\text{C}_6\text{H}_6$  with a few drops of piperidine, letting stand at a low temp. for a week and removing the  $\text{C}_6\text{H}_6$  by distn. under reduced pressure, orange crystals, m.  $118^\circ$ , sol. in NaOH with a brilliant red color. When the NaOH soln. was neutralized it was pptd. as a yellow mass, which melted indefinitely (approx.  $160^\circ$ ), with gas evolution; it is slightly sol. in water, giving a yellow soln., turning orange on adding NaOH. **XXIV**.  $\alpha$ -Pivalyl-5-nitrocoumarin, prepd. like **XXII** and recrystd. from MeOH, m.  $157.5-8.0^\circ$ , readily sol. in NaOH with orange-red, difficultly in water with yellow color, not very sol. in cold MeOH but quite sol. in warm MeOH and in  $\text{C}_6\text{H}_6$ . **XXV**. 1-Phenyl-3-*tert*-butyl-5-pyrazolone. **XXVI**. Bisphenyl-*tert*-butylpyrazolone. **XXVII**. 1-Phenyl-3-*tert*-butyl-4-methyl-5-pyrazolone. **XXVIII**. When **IX** and an excess of  $\text{NH}_4\text{OH}$  were heated in a sealed tube at  $120-30^\circ$  for 6 hrs., the product formed was identical with **VIII**, together with some trimethylaminocrotonic acid. **XXIX**. Pivalylacetonilide,  $\text{Me}_3\text{CCOCH}_2\text{CONHPh}$ .  $\text{PhNO}_2$  did not react with **IX** at room temp. An anilide was formed when the mixt. was heated in a sealed tube at  $160^\circ$  for 10 hrs. Et crotonate derivs. could not be detected in the products formed. Yield, 50%. It m.  $67^\circ$  (after 6 months  $82^\circ$ ), gives a blue-violet color with  $\text{FeCl}_3$ , sol. in org. solvents and in water, also in boiling ligroin, very sol. in NaOH. **XXX**. Ethyl isonitrosopivalylacetate,  $\text{Me}_3\text{CCOC}(\text{:NOH})\text{CO}_2\text{Et}$ . **IX** in glacial AcOH and the calcd. amt. of  $\text{NaNO}_2$  soln. were allowed to stand at a low temp. for 12 hrs. and then at room temp. for several days. An oil was obtained which could not be induced to cryst., crystals, m.  $92^\circ$ , formed spontaneously, however, after standing for several weeks. **XXXI**. *tert*-Butylisoxazalone,  $\text{Me}_3\text{CCC:N.O.CO.CH}_3$ , was formed by treating **IX** and an equal amt. of  $\text{PhNH}_2$  in

MeOH with  $\text{NH}_4\text{OH.HCl}$ . The reaction mixt. was extd. with  $\text{Et}_2\text{O}$ , from which crystals were obtained, m.  $106^\circ$ . **XXXII**. Ethyl pivalylacetate semicarbazone was prepd. by treating **IX** with  $\text{H}_2\text{NCONHNH}_2\text{HCl}$  and  $\text{AcONa}$ . After several days crystals were formed in the aqueous soln. Recrystd. from  $\text{Et}_2\text{O}$  they m.  $117^\circ$ . **XXXIII**.  $\gamma,\gamma,\gamma$ -Trimethyl- $\beta$ -hydroxybutyric acid. Prepn. **IX** was reduced by Na-Hg and the product formed recrystd. from  $\text{C}_6\text{H}_6$ ; it m.  $81.5^\circ$  (yield 60%),  $[\alpha]_D^{19} - 25^\circ \approx 2.0$ , sol. in EtOH,  $\text{Et}_2\text{O}$ , ligroin and warm  $\text{C}_6\text{H}_6$ , only slightly sol. in  $\text{H}_2\text{O}$ . At the end of the thesis there are mentioned several expts. in which the results were either negative or indefinite. These expts. pertained to reactions of **IX** with  $\text{PCl}_5$ ,  $\text{BzH}$ ,  $\text{AcCl}$ ,  $\text{HC}(\text{OEt})_3$ ,  $\text{Na}_2\text{SO}_4$ , HCN and urea.

A. R. ROSE

Chemistry of the heptane solution. II. Revision of the physical constants of heptane. F. KREMER and R. KREMER. *J. Am. Pharm. Assoc.* 9, 880-4 (1920); cf. C. A. 15, 730.—Fifteen specimens of the oleoresin of *Pinus sabiniana* were steam-

distd. The yield was 4.2–9.4%; av. 7.8%. The  $d_{20}$  of the distillates was 0.685 except one which was 0.686. The crude heptane was purified by successive shaking with concd.  $H_2SO_4$ , fuming  $H_2SO_4$ ,  $Na_2CO_3$  and  $KMnO_4$ . The constds. of the purified heptane were  $n_{20}$  1.3895;  $b_{760}$  97.33°;  $d_{20}$  0.68288;  $\gamma_{20}$  19.8 ergs;  $[\alpha]_D 0$ . L. E. WARREN

**Triphenylarsine and diphenylarsenious salts.** WM. J. POPE AND E. E. TURNER. *J. Chem. Soc.* 117, 1447–52 (1920).—In the prepn. of  $Ph_3As$ , yields may be increased from 67% (Michaelis and Reese, *Ber.* 15, 2876; Michaelis, *Ann.* 321, 160) to 95%, based on the  $PhCl$  used, by using  $C_6H_6$  instead of  $Et_2O$  as solvent. Most satisfactory results are obtained by covering 57 g. of Na (wire or slices) with 300 cc. of  $C_6H_6$  containing 1–2% of  $AcOEt$ , allowing to stand 30 min. to activate the Na, and running in slowly 85 g. of  $AsCl_3$  and 136 g. of  $PhCl$ , with cooling, after which the mixt. is boiled under reflux for several hrs., allowed to stand overnight, filtered, the inorg. residue washed with hot  $C_6H_6$ , and the filtrate and washings are distd. until the liquid shows 200°. The residue solidifies on cooling to almost pure  $Ph_3As$ . M. and R. showed that  $PhAsCl_2$  is formed by heating  $Ph_3As$  and  $AsCl_3$  under pressure, but P. and T. find pressure unnecessary. After slow addition of 25.5 g. of  $AsCl_3$  to 30.6 g. of  $Ph_3As$  maintained at 350°, and distn. under 12–15 mm., the fractions were (a) 120–60°, 17.7 g. of nearly pure  $PhAsCl_2$ ; (b) 160–200°, 22.2 g. of pure  $Ph_2AsCl$ ; (c) 200–250°, 2.2 g. of nearly pure  $Ph_3As$ , with a residue of 2.2 g. of  $Ph_3As$ . Increasing the time of adding the  $AsCl_3$  increases the proportion of  $Ph_2AsCl$ . On heating 15.3 g. of  $Ph_3As$  with 11.2 g. of  $PhAsCl_2$  for 4 hrs. at 300°, and distg. the pasty mass under 15 mm., 20 g. (80%) of  $Ph_2AsCl$  passed over. Boiling 12 g. of  $KOH$  in 10 cc. of  $H_2O$  and 200 cc. of alc. with 53 g. of  $Ph_2AsCl$  in 100 cc. of alc. for 1 hr., distg. off the solvent, and extg. with  $CHCl_3$ , gave a quant. yield of  $(Ph_2As)_2O$ , m. 89–91°. On heating the oxide at 100° with  $HBr$  in a sealed tube,  $Ph_2AsBr$  seps. as a colorless cryst. solid, m. 55–6°, described by Michaelis and La Coste (*Ann.* 201, 229) as a yellow oily liquid. The bromide is also obtained by heating  $AsBr_3$  with  $Ph_3As$ . *Diphenylarsenious iodide*,  $Ph_2AsI$ , is obtained by heating 25 g. of  $(Ph_2As)_2O$  with 30 g. of fuming  $HI$  in a sealed tube at 100° for 2 hrs. and recrystg. from  $C_6H_6$ , yellow cryst. scales, m. 45–6°. A less satisfactory method is the reaction of  $Ph_3As$  with  $AsI_3$ . M. R. SCHMIDT

**Residual affinity and coordination. III. Acetylacetones of selenium and tellurium.** GILBERT T. MORGAN AND HARRY D. K. DREW. *J. Chem. Soc.* 117, 1456–65 (1920).—Se and Te form with  $CH_3Ac$  a new class of compds. in which the bivalent radical  $C_6H_5O_2$  is associated with the metalloids. By treating 14.3 g. of  $SeCl_4$  in 140 cc. of dry  $Et_2O$  with 13 g. of  $CH_3Ac$  in 30 cc. of  $Et_2O$ , at ordinary temp.,  $HCl$  was evolved, the  $SeCl_4$  slowly went into soln., and a yellow ppt. appeared, which then dissolved to form a pale red fuming lachrymatory soln., which was evapd. at room temp. in an air current. The residue, chloroacetylacetone was driven off, was a pale red oil, which solidified on stirring and, recrystd. from  $C_6H_6$ , gave a 90% yield of pale primrose-yellow glistening plates or lath-like needles of *selenium acetylacetone*,  $(C_6H_5O_2)_2Se$ , (A), m. 175° (decompn.), in a sealed tube m. 185°. Mol. wts. in  $C_6H_6$  were 316 and 312, hence the double mol. was chosen for the formula. Any departure from the above method in solvents, temps. or proportions failed to give cryst. products.  $SeCl_4$  and  $CH_3BzAc$  apparently gave pale yellow *selenium benzoylacetone*, m. 212°. A has a faintly acid sweetish taste, is slightly sol. in hot  $H_2O$ , boiling  $Et_2O$ ,  $EtOH$ ,  $Me_2CO$ , or  $CHCl_3$ , and is more sol. in hot  $AcOH$ ; 100 cc. of boiling  $C_6H_6$  dissolve 1.5 g.; it is readily sol. in cold aq. alkali hydroxides or  $NH_4OH$  to bright yellow solns., which regenerate the compd. if neutralized at once with dil. acid. The alk. solns. soon decomp., deposit red Se, and evolve a nauseating odor. Prolonged treatment with  $Na_2CO_3$  gives the same decompn., the org. product being an oil with a pleasant ketonic odor. Dil. mineral acids are without effect; concd.  $HNO_3$  and  $H_2SO_4$  have a destructive

action, while concd. HCl gives quiet decompn. into red Se and chloroacetylacetone. FeCl<sub>3</sub> in H<sub>2</sub>O or alc. gives no red color after 2 hrs., but in 24 hrs. an orange tint appears, developed more quickly by boiling. Distn. with Zn dust gives rise to a nauseating odor, and forms Se and an oil with a ketonic odor. I in CHCl<sub>3</sub> has no action, but Cl gives SeCl<sub>4</sub> and chloroacetylacetone, while Br yields lachrymatory products and a colorless cryst. compd., m. 180°. Aq. H<sub>2</sub>S decomp. A in the cold with liberation of S and Se. Org. reducing agents cause a more or less rapid elimination of Se. Shaking 2 g. of A in powder with 3 g. of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in 18 cc. of H<sub>2</sub>O gave a colorless cryst. ppt. of *potassium selenodilithionate*, K<sub>2</sub>S<sub>2</sub>SeO<sub>6</sub>, scales, plates or needles from H<sub>2</sub>O, reddening at 190°, later evolving SO<sub>2</sub> and leaving a residue of K<sub>2</sub>SO<sub>4</sub>. Cold concd. soln. of NaHSO<sub>3</sub> with A gave *sodium selenodilithionate*, colorless lustrous scales, easily sol. in H<sub>2</sub>O, while aq. SO<sub>2</sub> and A gave CH<sub>3</sub>Ac<sub>2</sub>, extd. with Et<sub>2</sub>O, and *selenodilithionic acid*, which slowly decompd. into Se, SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>. The CH<sub>3</sub>Ac<sub>2</sub> set free in the above reactions was identified by its pale blue Cu and colorless Al derivs., and was estd. by coupling it with Na iso-*p*-nitrobenzenediazo oxide, NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>ONa.H<sub>2</sub>O, forming an orange-red ppt. of *p*-nitrobenzenediazoacetylacetone, m. 219-22°. The action of 7.6 g. (2 mols.) of CH<sub>3</sub>Ac<sub>2</sub> in 55 cc. of CHCl<sub>3</sub> on 10.3 g. of TeCl<sub>4</sub>, purified by sublimation, the orange soln. being heated on a water bath under reflux, gave HCl and a heavy dark gray oil, which was removed from the soln. and the latter concd. over CaO in a desiccator, giving a 62% yield of *tellurium acetylacetone dichloride*, C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>:TeCl<sub>2</sub>, sparingly sol. in Et<sub>2</sub>O, C<sub>4</sub>H<sub>4</sub> or CHCl<sub>3</sub>, easily sol. in Me<sub>2</sub>CO, from which it crystd. in large transparent hexagonal prisms; colorless needles from EtOH or C<sub>6</sub>H<sub>6</sub>; both forms darken at 155-60° and decomp. 169-73°, yielding Te and a lachrymatory oil. Mol. wt. detns. in Me<sub>2</sub>CO gave 241 and 255; calcd. 296.5. The salt does not become discolored by light. It readily loses Cl with hot H<sub>2</sub>O or aq. acids or alkalies, but boiling with aq. KOH does not set free Te. FeCl<sub>3</sub> develops a red color very slowly. An excess of warm aq. SO<sub>2</sub> gives Te and CH<sub>3</sub>Ac<sub>2</sub>. The dichloride, treated with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> or boiled with a slight excess of SO<sub>2</sub>, yielded *tellurium acetylacetone*, C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>:Te, heavy yellow needles, sparingly sol. in H<sub>2</sub>O, Et<sub>2</sub>O, CHCl<sub>3</sub> or EtOH, decompg. indefinitely at 145-80°, and subliming under reduced pressure at 160°. It resembles the Se compd. in its reactions. H<sub>2</sub>O<sub>2</sub> instantly decolorizes the yellow aq. soln., giving a white ppt., while H<sub>2</sub>S gives a black deposit (TeS<sub>2</sub>?); alc. HgI<sub>2</sub> produces a yellow ppt., and warm aq. SO<sub>2</sub> reduces the compd. with formation of Te. Quant. decompn. may be brought about by K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, an Al-Hg couple, and concd. HCl. The authors suggest the name "chelate" (from the great claw or "chela" of the lobster) to describe those caliper-like groups which function as two associating units and fasten upon a central metallic atom. Such groups are seen in the Co ethylenediamine compds. with CH<sub>3</sub>Ac<sub>2</sub>, where the group Me.CO.CH:-CMe.O forms a ring structure in which the metallic atom is involved. Other examples are given.

M. R. SCHMIDT

The formation of fatty acids by oxidation of paraffin. E. BÖRNSTEIN. *Brennstoff Chem.* 2, 61-3(1921).—A review of published work. W. B. V.

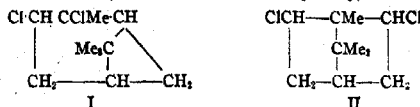
Chemistry of the polysaccharides. M. SAMER. *Biochem. Z.* 113, 255-6(1921).—Polematic concerning the article by Herzfeld and Klinger (*C. A.* 15, 99).

F. S. HAMMETT

Phthalic anhydride derivatives. ARTHUR LINZ. *J. Ind. Eng. Chem.* 13, 363(1921).—Additions to the list given in *J. Ind. Eng. Chem.* 13, 247; cf. Phillips, *C. A.* 15, 1029. E. J. C.

Chlorination of pinene. OSSIAN ASCHAN. *Öfversigt Finska Vetenskaps Soc.* 57, 14 pp. (1915).—The chlorination of pinene in the absence of moisture at -15° to 0° has been investigated; the results differ from any previously recorded. Chlorination occurs in a highly complex manner. The first fractions of the product give abundant solid

deposits of pinene hydrochloride. From the higher fractions only a *pinene dichloride* (II ?) was obtained, which may have been formed from a primary,



normally formed, unstable di-Cl-additive compd. (I). It forms transparent, rhombic, bipyramidal, plate-like crystals, m. 173–4°, b<sub>10</sub> 130°. In addition, a liquid dichloride b<sub>10</sub> 120–5° mm., which could not be isolated in the pure condition, is also produced. Neither dichloride is affected by boiling PhNH<sub>2</sub>. Preliminary expts. show that pinene hydrochloride can be readily chlorinated in CHCl<sub>3</sub> or CCl<sub>4</sub> until 4 additional atoms of H have been replaced. Colorless, cryst. products, m. 135°, 150–2°, and 130°, resp., have thus been obtained, analyses of which give results intermediate between those required for C<sub>10</sub>H<sub>15</sub>Cl<sub>3</sub> and C<sub>10</sub>H<sub>14</sub>Cl<sub>4</sub>; the formation of a dichloride was not observed.

J. C. S.

**Modified method for the preparation of α-sulfocarbonyl acids.** H. J. BACKER AND J. V. DUBSKY. *Rec. trav. chim.* 39, 694–8 (1920).—A more detailed account of work already published (*C. A.* 14, 1662).

J. C. S.

**The chlorine derivatives of methyl formate and carbonate.** V. GRIGNARD, G. RIVAT AND ED. URBAIN. *Ann. chim.* 13, 229–65 (1920).—See *C. A.* 14, 738–9.

HOMER ADKINS

**The catalytic oxidation of alcohols using metallic oxides and finely divided metals.** J. B. SENDRENS. *Ann. chim.* 13, 266–83 (1920).—The minimum temps. for the oxidation of the alcs. in the absence of a catalyst are about 450° for EtOH, 435° for iso-Bu and 410° for iso-Am alc., CO and H<sub>2</sub>O being the chief products. V<sub>2</sub>O<sub>5</sub>, Mo<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZnO, NiO, CuO, Al<sub>2</sub>O<sub>3</sub> were tried at temps. from 235° to 380°; ZnO and V<sub>2</sub>O<sub>5</sub> are the best catalysts, giving varying amts. of CO and CO<sub>2</sub> and small amts. of aldehyde and a little acid. Cu and CuO give the same gaseous products when used as catalysts with iso-AmOH at 235–240°. Mg or Al turnings become oxidized when they are used as catalyst with the lower alcs. but with iso-AmOH at 380° no oxidation takes place. Aldehyde and a little acid are produced. Finely powdered Zn, Al or Mg is not oxidized under the same conditions. Finely powdered Cu gives better yields of aldehyde and acid, and finely divided Ag still better. Ag at first gives much CO and little CO<sub>2</sub>; after a few hrs. the proportions are reversed. Ag<sub>2</sub>O was pptd. in porcelain and then reduced. Such a catalyst is the best one studied. 340° is the optimum temp.

HOMER ADKINS

**The ketimines.** CHAS. MOURRU AND GEORGES MIGNONAC. *Ann. chim.* 14, 322–59 (1920); cf. *C. A.* 7, 3114; 8, 3007, 3438.—Detailed directions are given for prep. ketimines previously described (*loc. cit.*) and also the following: *Phenylisopropyl*, b<sub>3</sub> 98–100°; *p-tolyethyl*, b<sub>3</sub> 94–96°, d<sub>4</sub><sup>18</sup> 0.9805; *phenylethylacetyl*, m. 126°; *phenylethylbutyryl*, m. 80–5°; *phenylethylisovaleryl*, m. 117°; *phenylethylbenzoyl*, m. 165°; *phenylpropylacetyl*, m. 115°; *phenylisobutylacetyl*, m. 134°; *phenylisobutylbenzoyl*, m. 160°; *propylphenylcarboxyethyl*, b<sub>35</sub> 190–192°; *diphenylcyclohexylcyclohexylidene ketisoketimine*, *di-p-tolyethylcyclohexylidene ketisoketimine*, b<sub>2,3</sub> 178–9°.

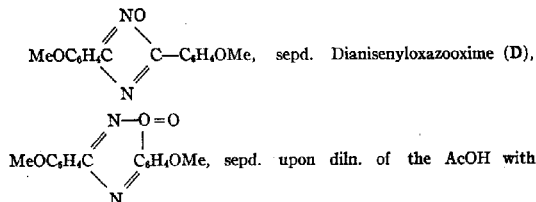
HOMER ADKINS

**The action of chlorine, hypochlorous acid and cyanogen chloride upon cyanamide and its derivatives.** CH. MAUGUIN AND L. J. SIMON. *Compt. rend.* 170, 998–1001 (1920).—Cl<sub>2</sub> gives with solid cyanamide (A) a yellow condensation product, infusible and insol. in H<sub>2</sub>O, EtOH, Me<sub>2</sub>CO, AcOH and alkali. The Ca salt of A in H<sub>2</sub>O with Cl<sub>2</sub> gave a lachrimatory product which spontaneously exploded after a few min. with the

destruction of the app.  $\text{Cl}_2$  with A in  $\text{H}_2\text{O}$  in presence of  $\text{ZnO}$  gives a ppt. which detonates on heating. An explosive and lachrimatory cryst. product was obtained by the action of  $\text{HClO}$  on A. In attempting to prepare  $\text{N}(\text{CN})_3$ , dry, finely powdered  $\text{C}:\text{NNAg}_2$  was slowly added with agitation at  $0^\circ$  to an excess of  $\text{CNCl}$ . A white compd.  $\text{AgN}(\text{CN})_2$  was obtained (explosive). Ag is sepd. from this compd. only by boiling  $\text{HNO}_3$ . On heating the compd. swells like  $\text{HgCNS}$ .  $\text{HCl}$  gas in  $\text{Et}_2\text{O}$  gives  $(\text{NC})_2\text{NH}\cdot\text{HCl}$  (B), which may be titrated (phenolphthalein) to  $(\text{NC})_2\text{NK}$ . B on heating gives biuret, and upon hydrolysis  $\text{NCNHCONH}_2$ , which is isolated by evapn. of the  $\text{H}_2\text{O}$ ; it is stable over  $\text{H}_2\text{SO}_4$  in *vacuo* and may be titrated. H. A.

The preparation of benzylamine by the catalytic hydrogenation of hydrobenzamide. GEORGES MIGNONAC. *Compt. rend.* 171, 1148-50(1920).—Hydrobenzamide (A) in abs.  $\text{EtOH}$  is agitated at  $15-18^\circ$  with catalytic Ni in an atm. of  $\text{H}_2$ . 4 atoms of  $\text{H}_2$  are introduced under atm. pressure. A mixt. of benzylamine (B) and benzalbenzylamine (C) is obtained by evapg. the solvent under reduced pressure at a low temp. A salt of B is obtained by hydrolysis of this mixt. with dil. acids. 20 g. A gave 5.5 g. of B. A upon reduction gives C and benzaldimine. This at higher temp. condenses with the loss of  $\text{NH}_3$ , giving A rather than being reduced to B. HOMER ADKINS

The oxidation of anisaldoxime and its peroxide. PAUL ROBIN. *Compt. rend.* 171, 1150-3(1920).—Anisaldoxime (A) was oxidized by the method described in C. A. 14, 176, giving the peroxide (B), insol. in  $\text{H}_2\text{O}$  and only slightly sol. in org. solvents, m.  $119-20^\circ$  (decompn.). 20 g. B was oxidized by the method described in C. A. 14, 404. The solvent was decanted from 12 g. of unchanged B and evapd. in the cold. The residue was washed with ether, thereby removing anisaldehyde (E) and anisonitrile (F). This was then dissolved in hot  $\text{AcOH}$ . Upon cooling dianisenyloxazooxime (C),



$\text{H}_2\text{O}$ . C recryst. from  $\text{EtOH}$  in long silky needles, m.  $135^\circ$ , sol. in  $\text{AcOH}$ , and rather sol. in ether and  $\text{C}_6\text{H}_6$ . D was dried at a low temp. and crystd. from  $\text{C}_6\text{H}_6$  in long silky needles, m.  $182^\circ$ . Crapdly becomes colored in the light, very sol. in  $\text{AcOH}$ , and slightly sol. in  $\text{Et}_2\text{O}$  and  $\text{C}_6\text{H}_6$ . D in  $\text{AcOH}$  sets free  $\text{I}_2$  from  $\text{NaI}$  and is reduced by  $\text{Zn} + \text{AcOH}$  to C and hydrolyzed by  $\text{Na}_2\text{CO}_3$  at  $100^\circ$ , according to the equation  $\text{D} = \text{F} + \text{MeOC}_6\text{H}_4\text{CO}_2\text{H}(\text{G}) + \text{NOH}$ . 25 g. of B boiled for a few hours in 250 cc.  $\text{C}_6\text{H}_6$  was completely decompd. giving A, D, C, E, F, G, and  $\text{N}_2\text{O}$ . A and D are first formed, D oxidizes A to E and is reduced to C. D decomp. in part as indicated above to give F and G and  $\text{N}_2\text{O}$ . Piperonaldoxime undergoes reactions similar to those indicated for A. HOMER ADKINS

Preparation of the methyl derivatives of the xylydines and of the naphthylamines by catalysis. ALPHONSE MAILHE AND F. DE GODON. *Compt. rend.* 171, 1154-5(1920).—A mixt. of 1 vol. of 2,3- $\text{Me}_2\text{C}_6\text{H}_3\text{NH}_2$  and 2 vols. of  $\text{MeOH}$  was passed over alumina at  $280-300^\circ$ . No primary base was found in the distillate but a mixt. of mono- and dimethylxylydine. With  $1/4$  less alc. similar results were obtained with 3,4- and 2,5- $\text{Me}_2\text{C}_6\text{H}_3\text{NH}_2$ . With 1 vol. of  $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$  and 4 vols. of alc., or 1 vol. of  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$  and 10 vols. of alc. similar results were obtained. HOMER ADKINS

**Some retro-pinacolic transpositions.** JEANNER LÄVY. *Compt. rend.* 172, 383-5 (1921).—The retro-pinacolic transposition takes place accompanying the dehydration of trisubstituted asym. primary or sec. alcs. according to the reaction  $R_3CCH(OH)R' \rightarrow R_3C:CRR' + H_2O$ . The hypotheses put forward to explain the mechanism of this reaction by Courier (1891), Klinger (1896), Zelinsky (1901), and A. Werner (1903) have been successively rejected. Tiffeneau, (*Bull. Soc. chim.* 35, 1156 (1906); 27, 459 (1920)) has proposed two interpretations: (1) the elimination of  $H_2O$  completely at the alc. C atom with the formation of a product of the type given above, and (2) the methylenic action of one of the R groups with the formation of a product of the type  $CH_2:CRCHRR'$ . By the exptl. dehydration of 2,2-diphenyl-3-butanol,  $b_{17}$  170° (giving 2,3-diphenyl-2-butene, m. 104-5°), 3,3-diphenyl-4-pentanol,  $b_{15}$  190° (giving 2,3-diphenyl-2-pentene,  $b_{160}$  297-9°), 2-methyl-2,3-diphenyl-3-propanol,  $b_{18}$  190° (giving 1,1-diphenyl-2-methylpropene,  $b_{160}$  280-2°), and 2,2,3-triphenyl-3-propanol, m. 121-2° (giving 1,1,2-triphenylpropene, m. 89-90°), L. shows that unless there is a shift of the double linkage T.'s 1st interpretation explains the facts. However, the work of Meerwein (*C. A.* 15, 854) has shown this is not the case with borneol. It is possible that the reagent employed for dehydration has an effect upon the final product. In L.'s work the dehydration was effected for the most part by heat alone.

O. B. H.

**The catalytic role of mercury in the sulfonation of anthraquinone.** A. ROUX AND CH. MARTINET. *Compt. rend.* 172, 385-7 (1921).—The sulfonation of anthraquinone (A) with hot fuming  $H_2SO_4$  gives the  $\beta$ - $SO_3H$  (B), but in the presence of Hg the  $\alpha$ -acid (C) can be obtained. In general the  $\alpha$ -derivs. of A are those most easily obtained by direct action. R. and M. hold that in the sulfonation of A without Hg the  $SO_3H$  group first enters the  $\alpha$ -position but on account of the high temp., etc., rapidly goes over to the  $\beta$ -position. The two important factors are (1) the velocity of sulfonation into the  $\alpha$ -position and (2) the velocity of transposition from the  $\alpha$ - to the  $\beta$ -position. At the temp. necessary to sulfonate A without a catalyst the two reactions are of the same order of velocity. In the presence of Hg the sulfonation of A can be carried out at lower temps. and yields than C. If the temp. is raised to that used for making B without a catalyst the product is still B in the presence of Hg, the yield being slightly improved. Further the action of heat alone is sufficient to convert C into B. The Na salt of C can be distinguished from that of B by its soly. in water (?), its ease of conversion into the corresponding Cl deriv. by the action of  $KClO_3$  and HCl and by the fact that it gives a ppt. with  $CuCl_2$  soln. [The abstractor's experience leads to the belief that the authors have confused the solubilities of the two salts.]

O. B. H.

**The pinacolic nature of some transpositions in the phenyldimethylglycol series.** M. TIFFENEAU AND ORÉKHOFF. *Compt. rend.* 172, 387-90 (1921).—When phenyldimethylglycol (A) is warmed with dil.  $H_2SO_4$  it loses water, and with phenylic migration forms phenyldimethylacetaldehyde (B):  $PhCH(OH)C(OH)Me_2 \rightarrow PhCHC-$



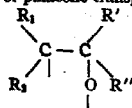
$Me_2 \rightarrow CHOCPhMe_2$ . The mono-Me ethers of A acted similarly. Dimethylstyrene oxide, in the presence of  $ZnCl_2$  or  $H_2SO_4$  isomerized with phenylic migration to give B. Dimethylstyrene iodohydrin gave with concd.  $AgNO_3$ , however, phenyl-2-butanone:  $PhCHIC(OH)Me_2 \rightarrow PhCHCMe_2$



$\rightarrow PhCHMeCOMe$ . Phenylic



transposition is only a special case of pinacotic transposition, i. e., when in the formula



R' is H and R'' is Ph.

O. B. H.

A new calcium salt. L. GAUCHER AND G. ROLLIN. *Compt. rend.* 172, 890(1921).—From EtCO<sub>2</sub>H and PI<sub>3</sub> G. and R. have prepd. *dipropiono-phosphorous acid* (HO<sub>2</sub>CCHMeO)<sub>2</sub>POH, the neutralization of which by chalk gives the *tricalcium salt* (C<sub>4</sub>H<sub>7</sub>O<sub>7</sub>)<sub>2</sub>Ca<sub>3</sub>.8H<sub>2</sub>O which is sol. in water and stable in neutral or acid solns. but in alk. soln. ppts. Ca<sub>3</sub>(PO<sub>3</sub>)<sub>2</sub>. The therapeutic properties will be studied.

O. B. H.

New preparation of amines by catalysis. ALPHONSE MAILHE. *Bull. soc. chim.* 27, 541-7(1920); cf. C. A. 14, 1964.—It was attempted to convert aldazines and ketazines into sym. hydrazines by H with Ni as catalyzer. But even at low temp., no such reaction took place, the principal products being primary amines formed by cleavage of the chain between the N atoms: (RCH:N-)<sub>2</sub> + 3H<sub>2</sub> = 2RCH<sub>2</sub>NH<sub>2</sub>. Small amts. of sec. and tert. amines also were formed, the lower the temp. the less of each. M. prepd. his aldazines and ketazines with N<sub>2</sub>H<sub>4</sub>. 2RCOR' + N<sub>2</sub>H<sub>4</sub> = (RR'C:N-)<sub>2</sub> + 2H<sub>2</sub>O. One part of N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O and 2 parts of aldehyde or ketone are either heated or cooled together, according to the speed of reaction, and EtOH is added if necessary to make them mutually sol. H<sub>2</sub>O is removed from the sepd. product by solid K. Eight aldazines and ketazines were prepd. and reduced catalytically: (1) Diethylidene-azine reduced at 140-50° gives primary, sec. and tert. ethylamines, the secondary predominating. (2) Diisobutylidene-azine reduced at 160° gives principally NH<sub>3</sub>, iso-BuNH<sub>2</sub> and (iso-Bu)<sub>2</sub>NH, with traces of primary amines. (3) Diisooamylidene-azine, prepd. from isovaleraldehyde by the method above, is an oil, b. 205-10°. By reduction at 180°, iso-AmNH<sub>2</sub> is the chief product, with traces of sec. and tert. amines. By reduction at 210-30°, the yield of sec. amine is twice that of primary iso-AmNH<sub>2</sub>, the tert. still only in small amt. (4) Dimethylketazine reduced at 150° forms iso-PrNH<sub>2</sub> in small amt., but chiefly (iso-Pr)<sub>2</sub>NH. (5) Diethylketazine reduced at 160-70° forms NH<sub>3</sub>, but chiefly 3-aminopentane, a liquid, b. 84°. The latter treated with PhNCO forms the compound PhNHCONHCHEt<sub>2</sub>, needles, sol. in EtOH, m. 148°. (6) Diisopropylketazine, prepd. from isobutyronone by the regular method, is a liquid, b. 175°. Reduced it gives mostly 2,4-dimethyl-3-aminopentane, a liquid, b. 125-7°. The latter treated with PhNCO forms the compound PhNHCONHCH(CHMe)<sub>2</sub>, white needles, m. 139-40°. (7) Dipropylketazine, prepd. from butyronone, is a liquid, b. 188°. Reduced at 170° it forms chiefly 4-aminoheptane, b. 135-6°. (8) Diisobutylketazine, prepd. from isovalerone, is an oil, b. 205-8°. Reduced at 215-30° it gives NH<sub>3</sub>, 2,6-dimethyl-4-aminohexane, b. 175-7°, and the major product, diisobutylisooamylamine, a liquid, b. 255-60°. HCl gives a cryst. hydrochloride.

C. C. DAVIS

2,6-Tetramethyldiaminoselenopyrnone. M. BATTEGAY AND G. HUGEL. *Bull. soc. chim.* 27, 557-60(1920).—In the action of fuming H<sub>2</sub>SO<sub>4</sub> with S in soln. on di-NH derivs. of Ph<sub>2</sub>NH, intense colors were found to be due to Se as impurity in the H<sub>2</sub>SO<sub>4</sub>. No color was produced with Se-free acid. This led the authors to replace free S in this reaction by Se compds., and to synthesize 3,6-tetramethyldiaminoselenopyrnone from (Me<sub>2</sub>NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub>. Procedure: 5 g. of Na<sub>2</sub>SeO<sub>4</sub> are dissolved in a few cc. of H<sub>2</sub>O, 80 cc. of monohydrated H<sub>2</sub>SO<sub>4</sub> is added, and the mixt. shaken to form fine crystals. This is added drop by drop to 150 cc. of H<sub>2</sub>SO<sub>4</sub> + 25% SO<sub>3</sub> at room temp. while shaking. Simultaneously is added fine dry (Me<sub>2</sub>NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub> fast enough to maintain a considerable excess, thus increasing the yield. The mixt. should stand 1.5 hrs. At no time should

the temp. exceed  $35^{\circ}$ . The liquor is poured on ice, an intense red forming, and the product then raised to boiling, the red changing to bluish. The soln. is filtered, and to the filtrate is added 54° B $\phi$ .  $\text{ZnCl}_2$  until the surface gives a metallic reflection. In 2 days a cryst. compd. settles, and this is filtered, dissolved in  $\text{H}_2\text{O}$  and reprecipitated by  $\text{ZnCl}_2$ . The mother liquor is blue, due to  $(\text{Me}_2\text{NC}_2\text{H}_4)_2\text{CHOH}$ . Yield, 8 g. of  $\text{C}_7\text{H}_7\text{N}_2\text{H}_5\text{SeCl}_2\cdot\text{ZnCl}_2$ . Its soln. in concd.  $\text{H}_2\text{SO}_4$  is claret, on diln. becoming blue.  $\text{H}_2\text{SO}_4 + 25\% \text{ SO}_3$  gives a red-brown soln. with yellow fluorescence. This on diln. with  $\text{H}_2\text{O}$  partly ppts.  $\text{NaOH}$  forms a reddish blue ppt., sol. in  $\text{Et}_2\text{O}$  with pink color with yellow fluorescence. The latter disappears in time and the soln. becomes yellow, acids making it red.  $\text{NH}_4\text{OH}$  reacts like  $\text{NaOH}$ , but the  $\text{Et}_2\text{O}$  soln. is yellow. Evapn. in  $\text{CO}_2$  gives a yellowish amorphous mass, m.  $115^{\circ}$ . The colored compds. from iodides and nitrates are slightly sol., those from dichromates insol. C. C. DAVIS

**Some propionitrile derivatives.** CHARLES MOUREU and RALPH L. BROWN. *Bull. soc. chim.* 27, 901 (1920); cf. Moureu, *Ann. chim. phys.* [7] 2, 191 (1894).— $\text{HOCH}_2\text{CH}_2\text{CN}$  (A),  $b_p$   $110^{\circ}$ , is obtained from  $\text{CH}_3\text{ClCH}_2\text{OH}$  and  $\text{NaCN}$  soln. in 86% yield (C. A. 11, 2333).  $\text{CH}_3\text{CHCN}$  (B), b,  $78^{\circ}$ , is obtained in 9 g. yield from 25 g. A and 90 g.  $\text{P}_2\text{O}_5$  mixed with 90 g. dry sand and distd. *in vacuo*.  $\text{CH}_3\text{BrCHBrCN}$ ,  $b_p$   $106-107^{\circ}$ , obtained from B and the theoretical wt. of  $\text{Br}_2$ ,  $d_4^{20}$  2.174,  $d_4^{25}$  2.140,  $n_D^{20}$  1.5452, mol. ref. 31.46 (calcd. 31.56), irritating to the mucous membrane.  $\text{CH}_3\text{BrCH}_2\text{CN}$ , colorless liquid,  $b_p$   $92^{\circ}$ , obtained from B by adding the theoretical amt. of dry  $\text{HBr}$ ,  $d_4^{20}$  1.6452,  $d_4^{25}$  1.6152,  $n_D^{20}$  1.4770, mol. ref. 23.44 (calcd. 23.69). Hydrolyzed with aq.  $\text{HBr}$  (d. 1.5) the compd. yielded  $\text{CH}_3\text{BrCH}_2\text{CO}_2\text{H}$ , m.  $61-2^{\circ}$ . Treated with excess of dry  $\text{HBr}$  the nitrile yielded a white solid, m.  $55-7^{\circ}$ , presumably  $\text{CH}_3\text{BrCH}_2\text{CN}\cdot\text{HBr}$ .  $\text{MeCHBrCN}$ , colorless liquid,  $b_p$   $59^{\circ}$ , slightly irritating to the mucus membrane, prepd. by dehydration of  $\text{MeCHBrCONH}_2$  with 1.2 parts by wt. of  $\text{P}_2\text{O}_5$  by distg. under reduced pressure and at  $250^{\circ}$  (crude yield, 85-90%),  $d_4^{20}$  1.5808,  $d_4^{25}$  1.5505,  $n_D^{20}$  1.4585, mol. ref. 23.61 (calcd. 23.69). With dry  $\text{HBr}$ , the nitrile formed  $\text{MeCHBrCN}\cdot\text{HBr}$ , m.  $64-5^{\circ}$  [*Ann.* 142, 65 (1867)], which on hydrolysis yielded  $(\text{MeCHBrCO})_2\text{NH}$ , m.  $148-9^{\circ}$ ,  $\text{HBr}$  and  $\text{NH}_4\text{Br}$ . R. L. BROWN

**The dissociation of ammonium carbamate.** C. MATIGNON and M. FREJACQUES. *Bull. soc. chim.* 29, 21-9 (1921); cf. C. A. 15, 671.—The dissociation of  $\text{NH}_4\text{CO}_2\text{NH}_4$  (A) has been studied at temps. at which the tension is less than atm. pressure. M. and F. have extended the study to higher temps. A was prepd. from  $\text{CO}_2$  and  $\text{NH}_3$  according to the equation:  $\text{CO}_2(\text{gas}) + 2\text{NH}_3(\text{gas}) = \text{CO}_2\cdot 2\text{NH}_3 + 39 \text{ cal.}$  (C. A. 2, 2474). A has a tension (dissociation) of 62 mm. Hg at  $20^{\circ}$ , increasing rapidly with the temp. A forms in the coldest part of the reaction vessel, and on the surface of the walls of the reaction coil and the accretion of salt hinders the heat exchange and the reaction is retarded. To obviate the difficulty,  $\text{CO}_2$  is lead into liquid  $\text{NH}_3$  and A forms in small brilliant leaves. The dissociation of A below  $100^{\circ}$  has been studied by Naumann (*Ann.* 160, 15 (1871)), by Horstmann (*Ann.* 187, 55 (1877); *Ber.* 9, 1625 (1876)) and Isambert (*Compt. rend.* 92, 919 (1881)). Engel and Moitessier (*Compt. rend.* 93, 595, 899 (1881)) have studied the dissociation at ordinary temp. and Fichter and Becker (C. A. 6, 750) at  $130-33^{\circ}$ . M. and F. measured the dissociation pressure at temps. at which the pressure was several atm. A used in the expts. was prepd. from  $\text{CO}_2$  and  $\text{NH}_3$  and the dissociation pressure at  $81^{\circ}$  was found to be 3.18 atm. A table is given showing the dissociation pressures at temps. between  $100^{\circ}$  and  $150^{\circ}$ . H. E. WILLIAMS

**Certain derivatives of crotonic aldehyde.** CHARLES MOUREU, MARCEL MURAT and LOUIS TAMPIER. *Bull. soc. chim.* 29, 29-34 (1921).—The authors in conjunction with war activities studied certain derivs. of crotonaldehyde (A) obtained from paraldehyde by Delépine's method (*Ann. chim. phys.* [8] 16, 136 (1909); cf. C. A. 3, 782). Lobry de Bruyn tried in vain to isolate  $\text{MeCH:CHCH(OH)CN}$  (B) from the product of the

action of HCN on A (*Bull. soc. chim.* **42**, 159(1884)) and Milton and Schaak (*Ann.* **299**, 34-9) obtained a liquid  $b_p$  132-6° when KCN and HCl acted on A in Et<sub>2</sub>O but the  $b_p$  is higher than that of the pure B now reported. Ultee's method has been successfully applied to A (*C. A.* **3**, 1536, 2701): 35 g. A and 18 . pure and dry HCN are mixed in a flask; cooled externally and 4 drops NaOH soln. are then added. In a few min. the mixt. boils owing to the heat liberated but should not be cooled. After 30 min. the reaction mixt. is acidified with H<sub>3</sub>PO<sub>4</sub> (helianthin), the excess of HCN distd. off and the residue distd. *in vacuo*, giving 46 g. B,  $b_p$  110-2°. The  $b_p$ s. for several pressures are given. B is a colorless liquid, viscous, odorless, has a burning taste, and is sol. in water, alc. and Et<sub>2</sub>O. On standing it becomes yellow and has the odor of HCN. B decomps. when distd. at atm. pressure. The temp. of decompn. was found to be 115°, and it decomps. when refluxed with dil. NaOH and with AgNO<sub>3</sub>. Zeisel (*Monatsh.* **7**, 359, 371(1886)) showed that A combined with Cl<sub>2</sub> in the cold and dark but he did not isolate any products.  $\alpha,\beta$ -Dichlorobutyraldehyde (C) results when 20 g. A in 100 g. CCl<sub>4</sub> at 0° are treated with dry Cl<sub>2</sub>; the liquid turns yellow. When the requisite amt. of Cl<sub>2</sub> is absorbed, the free Cl<sub>2</sub> is removed by air, HCl is removed by CaCO<sub>3</sub> and the filtrate is freed of CCl<sub>4</sub> and the residue C, 39.5 g.  $b_p$  58-60°, is a colorless liquid which loses HCl, turning brown. It has an odor resembling chloral. C decomps. when boiled under atm. pressure and is insol. in alc. Et<sub>2</sub>O, CHCl<sub>3</sub> and CCl<sub>4</sub>.  $\alpha$ -Chlorocrotonaldehyde (D) was obtained by Pinner (*Ann.* **179**, 31(1876)) and by Lieben and Zeisel (*Monatsh.* **4**, 531) in an impure state but may now be prepd. pure by treating C with NaOAc according to the method of Piloty and Stock (*Ber.* **31**, 1385(1898)). 65 g. C in 150 g. H<sub>2</sub>O with 150 g. NaOAc were treated with a current of steam until all the oil was distd. The lower layer, treated again with NaOAc and dried with Na<sub>2</sub>SO<sub>4</sub>,  $b_p$  53-4°. D is a colorless liquid, unstable in the light, has an irritating odor and is tear-producing, slightly sol. in H<sub>2</sub>O, sol. in alc., Et<sub>2</sub>O, CHCl<sub>3</sub> and CCl<sub>4</sub>. CH<sub>2</sub>:CH-CHClCHO, MeCH:CClCHO, and MeCCl:CHCHO may be made by removing HCl from C. M., *et al.*, concluded, *a priori*, that D had the structure MeCH:CClCHO and consequently it should add Cl<sub>2</sub> and yield MeCHClCClCHO.H<sub>2</sub>O, a deriv. of CCl<sub>4</sub>CHO.H<sub>2</sub>O employed as an hypnotic. To an iced CCl<sub>4</sub> soln. of D was added Cl<sub>2</sub> in CCl<sub>4</sub>. Addition took place at once with evolution of heat. A liquid,  $b_p$  160-5°, was obtained which with H<sub>2</sub>O gave croton-chloral, crystals from alc.,  $m.$  77-8°. Therefore, D had the structure MeCH:CClCHO. 10 g. D with 4 g. HCN and a few drops NaOH soln. were mixed and when added NaOH no longer caused an evolution of heat, H<sub>3</sub>PO<sub>4</sub> (helianthin) was added and the mixt. was distd. 11.6 g.  $\alpha$ -chlorocrotonaldehyde cyanohydrin,  $b_p$  137°, were obtained as a colorless product, with an odor of HCN, slightly sol. in H<sub>2</sub>O, sol. in alc., Et<sub>2</sub>O and CHCl<sub>3</sub>. It decomps. when distd. under atm. pressure.

H. E. WILLIAMS

**Esterification by zirconium oxide.** A. MAILHE AND F. DE GODON. *Bull. soc. chim.* **29**, 101-6(1921).—TiO<sub>2</sub> (Sabatier and M., *C. A.* **5**, 2091) is a better catalyst for esterifications than ThO<sub>2</sub>. A careful study of ZrO<sub>2</sub> now shows it to be as good as or better than TiO<sub>2</sub>. A tube 1.2 m. in length, containing 244 g. of catalyst, gave the best results, at 280-90°. Decreasing the rate of passage of the acid-alc. mixt., or increasing the proportion of alc., improved the yields decidedly. In the tube described a 1:1 (molar) mixt. of EtOH and AcOH gave, at 40 cc. per min., 71% of ester. A 4:1 mixt. gave up to 99% ester. Generally similar results are reported for PrOAc, Me<sub>2</sub>CHCH<sub>2</sub>OAc, Me<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>OAc, EtOOCBt, EtOOCPr, PrOOCPr, Me<sub>2</sub>CHCH<sub>2</sub>OOCPr, Me<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>OOCPr, EtOOCCHMe, and PrOOCCHMe. B. H. N.

**New method of preparation of secondary amines, and attempt to alkylate these bases.** A. MAILHE. *Bull. soc. chim.* **29**, 106-10(1921); *Compt. rend.* **172**, 280-3 (1921).—The hydrogenation of Schiff's bases to sec. amines in the vapor phase (M.,

C. A. 13, 2860) is frequently rather troublesome. By adding catalytic Ni to the liquid base, and passing a strong current of  $H_2$  while it is heated at  $160-80^\circ$ , excellent yields of sec. amines are obtained, without by-products, and within 0.5–1.0 hr. RNHPh ( $R = PhCH_2-$ ), m.  $36^\circ$ ;  $RNHCH_2H_4Me$ , o- m.  $55^\circ$ , m- b.  $312^\circ$ , p- b.  $310-2^\circ$ ;  $p-RNHCH_2H_4OMe$  m.  $64-5^\circ$ . *m*- and *p*- $RNHCH_2H_4Me$  with  $PhNCO$  gave *m*- and *p*- $RN(C_2H_5Me)-CONHPh$ , m.  $159^\circ$  and  $125-7^\circ$ , resp. The method of M. and de Godon (C. A. 12, 1383, 1550) for methylating aromatic amines is not applicable to these products, as they break down when their vapors, mixed with MeOH, are passed over  $Al_2O_3$  at  $380-400^\circ$ , RNHPh giving, e. g., PhMe and PhNMe<sub>2</sub>. The necessary H comes from the MeOH with  $H_2CO$  formation, and the  $PhNH_2$  formed is at once methylated. This reaction is typical.

BEN H. NICOLET

Effect of reducing agents on tetranitromethane, and a rapid method of estimation. ALBEN BAILLIE, ALEXANDER KILLEN MACBETH AND NORAH IRENE MAXWELL. *J. Chem. Soc.* 117, 880–4 (1920).—One  $NO_2$  group in tetranitromethane (A) differs from the others in its behavior on hydrolysis (cf. C. A. 9, 1037). The action of alk. reducing agents is described and data on electrical reduction are promised. In solns. containing sufficient KOH to keep the reaction alk.,  $Na_2SO_3$ ,  $K_2SO_3$ ,  $NaKC_2H_3O_6$ ,  $Na_3AsO_3$ ,  $Na_3PO_3$ , and  $N_2H_4$  give smooth reduction, with good yields of the K salt of nitroform (B).  $(NH_4)_2S$  gives more complicated products. The reaction with  $N_2H_4$  yields 0.5 mol.  $N_2$  for each mol. of A used, and can be used as a quant. method (accuracy at least 1%) for A alone or in the presence of B,  $HNO_3$ , or  $HNO_2$ . The detns. were made in a Lunge nitrometer. The gas is evolved very rapidly, and provision must be made for this.

BEN H. NICOLET

The dehydroxydation of aldehydes. Mechanism of their oxidation. ERICH MÜLLER. Dresden. *Ann.* 420, 241–61 (1920).—Acids and gaseous H may be formed in the electrochem. or chem. oxidation of  $HCHO$ ,  $AcH$ , and  $BzH$  in alk. soln. This reaction is called *dehydroxydation*. If this is carried out with  $CuO$ ,  $Cu_2O$  or  $Ag_2O$ , there is an incubation period. Even without special oxidation agents, an alk.  $HCHO$  soln. evolves H in small amts. by the action of certain metals. These same metals accelerate the Cannizzaro reaction. The mechanism of the oxidation may be represented by the following scheme: (I)  $RCH(OH)_2 + F \longrightarrow RCH(:O)OH + H^+$ ; (II)  $RCH(:O)OH + F \longrightarrow RCOOH + H^+$ ; (III)  $RCH(:O)OH \longrightarrow RCOOH + H(\longrightarrow H_2)$ ; (IV)  $RCOOH + F \longrightarrow RCOOH$ . [Reaction IV is given thus twice in the original. It is not made evident what this is intended to represent].  $F$  is the charge supplied by the elec. current or by the oxidizing agents. In the oxidation of aldehydes there result accordingly primarily *O*-aldehydes. (By this term M. designates the oxidation product of aldehyde containing an over-satd. C atom.) If these decomp. more rapidly according to III than according to II, *dehydroxydation* is observed. The transformation of aldehyde into acid without evolution of H may proceed according to  $I \longrightarrow II$  as well as by  $I \longrightarrow III \longrightarrow IV$ . Whether the oxidation of the aldehyde in the presence of catalyzers causes the evolution of H depends upon whether these catalyzers accelerate III more than IV. C. J. WAST.

Arylazoglyoxalinecarboxylic acids. ROBERT GEORGE FARGHER. Wellcome Chem. Research Lab. *J. Chem. Soc.* 119, 158–64 (1921); cf. C. A. 13, 1301; 14, 3219.—In view of the importance of the 4-arylazoglyoxaline-5-carboxylic acids as intermediate compds. in the synthesis of the purine ring from the glyoxaline nucleus, the reaction has been submitted to further examn. The same product is obtained from the di- or mono- $CO_2H$  acid. Upon reduction with cold  $SnCl_2$  soln., the  $CO_2H$  grouping is eliminated and the acids yield the same products as the corresponding non-carboxylated glyoxalines. In certain cases, however, the acid may be obtained. 4-*p*-Bromobenzene-azo-2-phenylglyoxaline-5-carboxylic acid,  $C_{18}H_{11}O_3N_2Br$ , is prepd. by diazotizing 6.8

g.  $p$ - $\text{BrC}_6\text{H}_4\text{NH}_2$  in 130 cc. 10% HCl with 2.88 g.  $\text{NaNO}_2$  and adding this to 9.23 g. 2-phenylglyoxaline-4,5-dicarboxylic acid (A) in 400 cc.  $\text{H}_2\text{O}$  containing 67.2 g. cryst.  $\text{Na}_2\text{CO}_3$ . The Na salt is purified by crystn. from  $\text{H}_2\text{O}$  and the acid liberated and crystd. from alc. It forms glistening red needles, which darken at  $160^\circ$  and m.  $210^\circ$  (decompn.). (All m.p.'s are cor.) The  $\text{H}_2\text{SO}_4$  soln. has an eosin-red color. The sodium salt,  $\text{C}_{18}\text{H}_{13}\text{O}_5\text{N}_2\text{BrNa} \cdot 3\text{H}_2\text{O}$ , forms a felted mass of orange needles. The same product was obtained by using 2-ph nylglyoxaline-4-carboxylic acid. Reduced by triturating 4 g. in 25 cc. concd. HCl with 14 cc.  $\text{SnCl}_4$  soln.,  $\text{CO}_2$  was evolved and 5 amino-4-[2'-amino-5-bromophenyl]-2-phenylglyoxaline obtained. Monoacetate,  $\text{C}_{18}\text{H}_{17}\text{N}_2\text{Br} \cdot \text{C}_4\text{H}_7\text{O}_2$ , prepd. by adding  $\text{AcONa}$  to the base and crystg. from a little  $\text{AcOH}$ , minute needles, m.  $161^\circ$ .  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  gave a gray ppt., which darkened when the soln. was warmed. Excess of  $\text{H}_2\text{SO}_4$ , added to the concd. soln. of the HCl salt, gave the sulfate, minute, flattened prisms. Reduction with  $\text{Na}_2\text{S}_2\text{O}_4$  gave a 52% yield of  $p$ - $\text{BrC}_6\text{H}_4\text{NH}_2$ . 4- $p$ -Bromobenzeneazo-2-methylglyoxaline-5-carboxylic acid,  $\text{C}_{11}\text{H}_7\text{O}_5\text{N}_2\text{Br}$ , was prepd. in a similar manner, and purified by crystg. the free acid from alc., orange needles with 0.5  $\text{H}_2\text{O}$ , which darken rapidly above  $160^\circ$ . The concd.  $\text{H}_2\text{SO}_4$  soln. is orange-red. It yields, on reduction with  $\text{SnCl}_4$ , 2-methyl-4-[2'-amino-5'-bromophenyl]-5-glyoxaline-HCl. 2- $p$ -Bromobenzeneazoglyoxaline-4,5-dicarboxylic acid,  $\text{C}_{11}\text{H}_7\text{O}_5\text{N}_2\text{Br}$ , bunches of minute, red needles, m.  $250^\circ$ . From alc., it contains 1  $\text{C}_2\text{H}_5\text{O}$ . Upon reduction, 2- $p$ -bromobenzenehydrazoglyoxaline-4,5-dicarboxylic acid,  $\text{C}_{11}\text{H}_9\text{O}_5\text{N}_2\text{Br}$ , is formed, decomp.  $203^\circ$ ; dil.  $\text{H}_2\text{O}_2$  gives a reddish brown color,  $\text{FeCl}_3$  a turbid orange soln. and warm dil.  $\text{HNO}_3$  a bright yellow color. Upon nitration of A, 2- $m$ -nitro, phenylglyoxaline-4,5-dicarboxylic acid (?),  $\text{C}_{11}\text{H}_7\text{O}_5\text{N}_3$ , is formed, small needles, decomp.  $266^\circ$ . There seems to be no tendency to displace the  $\text{CO}_2\text{H}$  group by the  $\text{NO}_2$  group. The corresponding amino acid  $\text{C}_{11}\text{H}_9\text{O}_5\text{N}_3 \cdot 2\text{H}_2\text{O}$  is obtained by reduction; after treatment with  $\text{HNO}_3$ , it developed a deep red color with  $\beta$ - $\text{C}_{10}\text{H}_7\text{ONa}$ . C. J. WEST

The constitution of catechin. III. Synthesis of acacatechin. MAXIMILIAN NIERENSTEIN. Univ. Bristol. *J. Chem. Soc.* 119, 164-70(1921); cf. C. A. 15, 233. —A suspension of 5 g. 3,4,2',4',6'-pentamethoxydiphenylmethyl chloromethyl ketone (A) in 50 cc.  $\text{H}_2\text{O}$ , heated vigorously for 32 hrs. with 20 g.  $\text{NaHCO}_3$ , gave  $\omega$ -hydroxy-3,4,2',4',6'-pentamethoxy- $\alpha,\alpha$ -diphenylpropan- $\beta$ -one,  $\text{C}_{21}\text{H}_{21}\text{O}_7$ , small prismatic needles from alc., m.  $121-2^\circ$ . 5 g. of this compd. in 50 cc.  $\text{Ac}_2\text{O}$ , heated 8 hrs. on a  $\text{H}_2\text{O}$  bath with 25 cc. of a soln. of 4.32 g.  $\text{AcCl}$  in 100 cc.  $\text{Ac}_2\text{O}$ , gave 4,6,3',4'-tetramethoxy-3-phenylchroman-2-one (B),  $\text{C}_{19}\text{H}_{19}\text{O}_6$ , small pointed needles from abs. alc., m.  $146-7^\circ$ . B is also obtained by heating 5 g. A in 75 cc. dry  $\text{C}_6\text{H}_6$  with 0.1 to 0.3 g.  $\text{AlCl}_3$  on a  $\text{H}_2\text{O}$  bath for 12-16 hrs. Phenylhydrazone,  $\text{C}_{23}\text{H}_{23}\text{O}_6\text{N}_2$ , yellow needles from  $\text{AcOH}$ , decomp.  $236-9^\circ$ . Upon reduction with Na and alc., B gives 3,4,2',4',6'-pentamethoxy- $\alpha,\alpha$ -diphenylpropane(C). 3 g. B, in 75 cc.  $\text{Ac}_2\text{O}$ , heated 5 hrs. at  $100^\circ$  with 20 g. Zn dust, gives 2-hydroxy-4,6,3',4'-tetramethoxy-3-phenylchroman (D), m.  $152-3^\circ$ . This compd. is identical with Perkin's acacatechin tetra-Me ether, with the exception that it does not give the indigo-blue color with  $\text{AcOH-HNO}_3$ .  $\text{FeCl}_3$  gives a violet color when added to a suspension in concd.  $\text{H}_2\text{SO}_4$ . This is due to the 3-phenylchroman nucleus. On reduction with Na and alc. and subsequent methylation, D yields C. 4 g. D in 70 cc.  $\text{AcOH}$ , heated in a sealed tube for 6 hrs. with 4 g.  $\text{AcCl}$ , gave 2,4,6,3',4'-pentahydroxy-3-phenylchroman, which is identical with Perkin's acacatechin (*J. Chem. Soc.* 81, 1169(1902); 87, 398(1905)). C. J. WEST

Influence of colloids on the rate of reactions involving gases. I. Decomposition of hydroxylamine in the presence of colloidal platinum. ALEXANDER FINDLAY AND WILLIAM THOMAS. *J. Chem. Soc.* 119, 170-6(1921).—Findlay and King have shown (C. A. 8, 3734) that the rate of escape of gas from a supersatd. soln. is influenced by the presence of colloids. The study has now been extended, in a preliminary way,

to ascertain the influence of colloids on the velocity of a reaction in which a gas is evolved. The reaction chosen was the decompn. of  $\text{NH}_4\text{OH} \cdot \text{HCl}$  in alk. soln. in the presence of colloidal Pt (cf. Tanatar, *Z. physik. Chem.* **40**, 475(1902)). The colloids used were dextrin, starch, gelatin peptone and  $\text{Fe}(\text{OH})_3$ . The reaction mixt. was chosen as follows: 100 cc. Pt soln. (Bredig), 1 g.  $\text{NH}_4\text{OH} \cdot \text{HCl}$  and 10 cc.  $\text{NaOH}$  soln. (60 g. in 100 cc.  $\text{H}_2\text{O}$ ). The  $\text{NH}_4\text{OH} \cdot \text{HCl}$  and the added colloid were dissolved in the Pt sol, a const. rate of stirring and temp. obtained, the alkali was added and the readings were begun after 2 min. The effect of the colloids is seen in the vol. of gas evolved after 40 min.: No colloid, 40.35 cc.; dextrin, 1%, 31.75; 2%, 21.00; 3%, 15.20; starch, 1%, 37.60; 2%, 32.50; 3%, 28.00; gelatin, 1%, 16.25; 3%, 12.85; 5%, 9.92; peptone, 0.25%, 7.30; 0.1%, 9.50. The data are insufficient to discuss the effect of colloids on the rate of reaction but two different explanations are temporarily offered. C. J. Warr

**Dihydroxynaphthaldehydes.** GILBERT T. MORGAN AND DUDLEY CLEOTE VINING. Univ. Birmingham. *J. Chem. Soc.* **119**, 177-87(1921).—The ten  $\text{C}_{10}\text{H}_6(\text{OH})_2$  have been submitted to the HCN synthesis for aldehydes, with the result that each of the isomers has been found to condense with 1 mol. of the reagent. In this condensation the  $\text{C}_{10}\text{H}_6(\text{OH})_2$  display greater reactivity than the three  $\text{C}_8\text{H}_6(\text{OH})_2$ , only 1 of which (resorcinol) undergoes the Gatterman condensation. In general, 10 g. fused  $\text{ZnCl}_2$  were added to 50 cc. dry  $\text{Et}_2\text{O}$  in a closed vessel and allowed to stand until soln. resulted, 10 g.  $\text{C}_{10}\text{H}_6(\text{OH})_2$  and 8 cc. HCN were added and a rapid stream of HCl was passed in with stirring. The oil which sepd. was washed with  $\text{Et}_2\text{O}$  and warmed, when the aldehyde sepd. *3,4-Dihydroxy-1-naphthaldehyde*,  $\text{C}_{10}\text{H}_6\text{O}_2$ , minute, pale yellow needles from  $\text{Et}_2\text{O}$ -petr. ether, m. 178-80°; yield 21%. *p-Bromophenylhydrazone*,  $\text{C}_{11}\text{H}_9\text{O}_2\text{N}_2\text{Br}$ , yellow needles from alc., m. 137-8°. *3,4-Dihydroxynaphthylideneaniline*,  $\text{C}_{17}\text{H}_{11}\text{O}_2\text{N}$ , deep red needles with a green reflex, m. 200-2°. *2,4-Dihydroxy-1-naphthaldehyde*, needles from  $\text{C}_6\text{H}_6$ -petroleum, purplish brown, acicular prisms from alc., m. 214°. Yield, 42%. *p-Bromophenylhydrazone*, yellow needles from alc., m. 165.5-6.5°. *2,4-Dihydroxy-1-naphthylideneaniline*, lemon-yellow needles, changing to red at 245° and m. 252°. *1,4-Dihydroxy-2-naphthaldehyde*, in 13% yield, silky, greenish yellow, felted needles from dil. alc. or  $\text{H}_2\text{O}$ , m. 188-90°. *p-Bromophenylhydrazone*, dark green scales from dil. AcOH or alc., decomp. 214°. This gives an intense bluish red soln., becoming bluer on diln. *1,4-Dihydroxy-2-naphthylideneaniline*, dark red, feathery needles from alc., m. 184-5°. *2,3-Dihydroxy-1-naphthaldehyde*, obtained in 62% yield, yellow, acicular prisms, m. 133.5-4.5°. *p-Bromophenylhydrazone*, lustrous yellow scales, m. 200° (decompn.). *2,3-Dihydroxy-1-naphthylideneaniline*, lustrous, lemon-yellow needles from alc., m. 199-200°. *4,8,1-C\_{10}H\_5(\text{OH})\_2\text{CHO}* (Gattermann, *C. A.* **2**, 820), minute, yellow needles, blacken 280°, does not m. 300° (G. gives 195-215°). *p-Bromophenylhydrazone*, lustrous, golden yellow scales, m. 206° (decompn.). The  $\text{PhNH}_2$  deriv. m. 200° (G., 194-5°). *4,5-Dihydroxy-1-naphthaldehyde*, insol. in light petroleum, lemon-yellow, nodular crystals, m. 164-6° (decompn.). Yield, 24%. *p-Bromophenylhydrazone*, brownish yellow, felted needles, m. 180° (decompn.). *4,5-Dihydroxy-1-naphthylideneaniline*, dark red needles with slight green reflex, darkens 200°, does not m. 280°. A by-product of this aldehyde is a 1,8-dihydroxy-2-naphthaldehyde (?), sparingly sol. in light petroleum and sepd. from its isomer by extrn. with petroleum, m. 134-5°; yield, 0.8%. *p-Bromophenylhydrazone*, lemon-yellow, decomp. 181°. *Dihydroxynaphthylideneaniline*, reddish golden yellow needles, m. 229-30°. *2,6,1-C\_{10}H\_5(\text{OH})\_2\text{CHO}*, dark yellow acicular prisms, m. 189-90° (G., 185-90°). *p-Bromophenylhydrazone*, minute yellow scales from alc., m. 194-5°. The  $\text{PhNH}_2$  deriv. m. 250-60° (G., 215-35°). *2,7-Dihydroxy-1-naphthaldehyde*, in 70% yield, pale yellow, felted needles, m. 166.5-8.5° from dil. alc. (contains 0.5  $\text{H}_2\text{O}$ ), or 159.5-60.5° from  $\text{C}_6\text{H}_6$ . *p-Bromophenylhydrazone*, shimmering, greenish yellow scales, m. 202-3° (de-

compn.). *2,7-Dihydroxy-1-naphthylideneaniline*, lustrous, yellow needles, m. 214–5°. The product described by G. is probably the 4,7-deriv.  $1,6\text{-C}_{10}\text{H}_4(\text{OH})_2$  gives 2 products. *4,7-Dihydroxy-1-naphthaldehyde*, in 64% yield, prismatic, silvery needles from alc., yellowish brown by transmitted light and green by reflection, or silvery white needles with yellowish brown tint from  $\text{H}_2\text{O}$  (both products with 1  $\text{H}_2\text{O}$ ), darkens 160°, decomp. 218°. *p-Bromophenylhydrazone*, golden yellow needles from dil. alc., decomp. 185°. *4,7-Dihydroxy-1-naphthylideneaniline*, orange-red scales with green reflex, from alc., darkens 240°, did not m. 280°. *2,5-Dihydroxy-1-naphthaldehyde* (yield, 21%), sepd. by extrn. with  $\text{CHCl}_3$ , bright yellow needles, decomp. 225–30°. *p-Bromophenylhydrazone*, yellow needles with 1  $\text{H}_2\text{O}$  from alc., m. 206–7° (decompn.). *2,5-Dihydroxy-1-naphthylideneaniline*, golden orange needles, m. 209–10°. A third possible isomer m. 179–84° and gave a Schiff base, orange-yellow needles, m. 244–6°. *4,6-Dihydroxy-1-naphthaldehyde*, from  $1,7\text{-C}_{10}\text{H}_6(\text{OH})_2$ , insol. in dry  $\text{C}_6\text{H}_6$ , yellow microneedles from  $\text{H}_2\text{O}$ , decomp. 265–70°. *p-Bromophenylhydrazone*, greenish yellow scales with silvery luster, m. 205–6° (decompn.). The anil forms a dark red cryst. product, decomp. 230–40°. *2,8-Dihydroxy-1-naphthaldehyde*, shining yellow scales, decomp. 203–4°. *p-Bromophenylhydrazone*, minute, bright yellow needles, m. 106–7° (decompn.). *2,8-Dihydroxy-1-naphthylideneaniline*, lustrous, golden orange needles, darken 240°, do not m. 280°.

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**o-Chlorodinitrotoluenes. II. GILBERT T. MORGAN AND LESLIE AMIEL JONES.** Univ. Birmingham. *J. Chem. Soc.* 119, 187–92(1921); cf. C. A. 14, 2782.—*2,4,6-Cl-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Me*, recently isolated from the nitration products of *2,4-Cl(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Me*, has now been obtained to a similar extent in the nitration of *2,6-Cl(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Me*. This is sepd. by crystg. the 5,6-di- $\text{NO}_2$  compd. from concd.  $\text{H}_2\text{SO}_4$ , dilg. the filtrate with  $\text{H}_2\text{O}$  and crystg. the oil from alc. The total yield is between 5 and 10%. *Benzene-5-azo-6-chloro-2,4-tolylenediamine*,  $\text{C}_{12}\text{H}_{12}\text{N}_4\text{Cl}$ , by reducing the  $\text{NO}_2$  compd. and treating with 1 mol.  $\text{PhN}_2\text{Cl}$ , stout red prisms from  $\text{C}_6\text{H}_6$  and petroleum, m. 160°. The dihydrochloride, dark red. Diacetate, silky orange needles from alc., decomp. 276°. *Bis-azo compound*,  $\text{C}_{16}\text{H}_{11}\text{N}_8\text{Cl}$ , by using an excess of  $\text{PhN}_2\text{Cl}$ , bright red flakes, m. 192°, crysts. unchanged from  $\text{Ac}_2\text{O}$ . *4-Nitrobenzene-5-azo-6-chloro-2,4-tolylenediamine*,  $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_4\text{Cl}$ , dark reddish black prisms with green reflex from acetone, decomp. 240–5°. Diacetate,  $\text{C}_{17}\text{H}_{10}\text{O}_4\text{N}_4\text{Cl}$ , red, acicular prisms, decomp. 290°. These azo compds. give varying shades of orange-red in cold concd.  $\text{H}_2\text{SO}_4$ . *6-Chloro-4-nitro-N-methyl-m-toluidine*,  $\text{C}_8\text{H}_9\text{O}_2\text{N}_2\text{Cl}$ , by passing dry  $\text{MeNH}_2$  into the 4,5-di- $\text{NO}_2$  compd. in abs. alc. at 15°, deep red, acicular prisms, m. 127°. The constitution was proved by methylating the toluidine. *Nitrosamine*,  $\text{C}_8\text{H}_9\text{O}_2\text{N}_3\text{Cl}$ , yellow plates, m. 70°. *6-Chloro-3-nitro-N-methyl-o-toluidine*, from the 5,6-di- $\text{NO}_2$  compd., orange acicular prisms, m. 84–7°. *Nitrosamine*, pale yellow prismatic needles, m. 86–7°. *6-Chloro-4-nitro-N-phenyl-m-toluidine*,  $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}$ , by heating  $\text{PhNH}_2$  and the 4,5-di- $\text{NO}_2$  compd. in alc. 36 hrs., reddish orange, rectangular pyramids, m. 95–6°. The same product was obtained by heating the toluidine with  $\text{PhBr}$ ,  $\text{K}_2\text{CO}_3$  and  $\text{CuI}$ . *Nitrosamine*, yellow prisms, m. 95–6°. *6-Chloro-3-nitro-N-phenyl-o-toluidine (A)*, orange rhomboidal plates, m. 108–9°. The reaction proceeds for several weeks. *Nitrosamine*, yellow prisms, m. 91°. *6-Chloro-3-phenyl-3,4-tolylenediamine*, by the reduction of A with  $\text{Zn}$  and  $\text{NH}_4\text{Cl}$ , pink needles, m. 109.5°. The diazoimine,  $\text{C}_{13}\text{H}_{10}\text{N}_7\text{Cl}$ , was formed by adding  $\text{NaNO}_2$  to a glacial  $\text{AcOH}$  soln., silky, pink needles, m. 119–20°. *6-Chloro-2-methyl-2,3-tolylenediamine hydrochloride*, fine needles. The free base is an oil. *Diazoimine*, flesh-colored, prismatic needles, m. 238–40°. Thus in the case of the 5,6-di- $\text{NO}_2$  compd. the basic radical displaces the  $\text{NO}_2$  group in position 6 and not the 5- $\text{NO}_2$  group situated in a sympathetic position with respect to the Cl and the other  $\text{NO}_2$  group.

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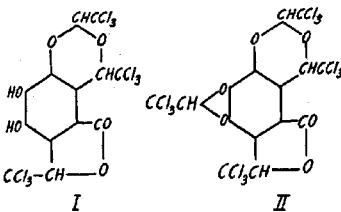
The constitution of the disaccharides. V. Cellobiose (cellulose). WALTER NORMAN HAWORTH AND EDMUND LANGLEY HIRST. Univ. St. Andrews. *J. Chem. Soc.* 119, 193-201 (1921); cf. *C. A.* 14, 1821.—The formula for cellobiose proposed in *C. A.* 13, 2856, has been confirmed:  $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CHO}$ .

$\text{CH}(\text{CH}_2\text{OH})\text{CHCH}(\text{OH})\text{CH}(\text{OH})\text{CHOH}$ . Cellobiose is conveniently prepd. as follows:

20 g. dry filter paper are stirred into a  $\text{H}_2\text{O}$ -cooled mixt. of 80 cc.  $\text{Ac}_2\text{O}$  containing 11 cc. concd.  $\text{H}_2\text{SO}_4$ , till a viscid paste is formed (5 min.). The paste is then heated in a  $\text{CaCl}_2$  bath at  $120^\circ$ , which caused rapid disintegration of the paper; at  $112^\circ$  a dark red, mobile liquid results. As soon as the red soln. appears to be changing to black, the whole is poured into 1.5 l. cold  $\text{H}_2\text{O}$ . After 6 hrs. the pale yellow ppt. is filtered and dried at  $40^\circ$ , then crystd. from 300 cc. 90% EtOH. The yield of octaacetate was about 25-30% of the wt. of filter paper. The Ac groups were removed by hydrolysis with KOH. In the methylation, the free sugar was not isolated. K cellobiosate (11 g.) in a little  $\text{H}_2\text{O}$  was treated with 38 cc.  $\text{Me}_2\text{SO}_4$  and 36 g. NaOH in 70 cc.  $\text{H}_2\text{O}$ . The product consisted essentially of a liquid,  $b_{\text{D}}^{20} 200^\circ$ ,  $n_{\text{D}} 1.4687$ , and analyzed for hexamethylmethylcellobioside,  $\text{C}_{18}\text{H}_{36}\text{O}_{11}$ . This, upon treatment with  $\text{Ag}_2\text{O}$  and MeI, gave the heptamethyl derivative,  $\text{C}_{20}\text{H}_{38}\text{O}_{11}$ ,  $b_{\text{D}}^{20} 190-200^\circ$ ,  $m. 76-78^\circ$ ,  $n_{\text{D}} 1.4643$ ,  $[\alpha]_{\text{D}}^{20} 9^\circ$  in  $\text{H}_2\text{O}$  ( $c. 1.560$ ),  $9.9^\circ$  in acetone ( $c. 1.805$ ). Upon hydrolysis with 5% HCl for 5 hrs. at  $80-95^\circ$ , about equal amts. of butylene-oxidic tetramethylglucose and trimethylglucose were isolated. The later was identical with that isolated from methylated cellulose and methylated lactose,  $m. 115-6^\circ$ . The oxidic structure of the latter was confirmed by methylating with MeI and  $\text{Ag}_2\text{O}$ ; the process had to be repeated 6 times to obtain a 92% yield of the tetra-Me deriv. From a comparison of lactose and cellobiose, the latter may be considered as glucose- $\beta$ -glucoside.

C. J. WEST

Derivatives of gallic acid. II. Gallic acid (and the cresotic acids) and chloral. RUPCHAND L. ALIMCHANDANI AND ANDREW NORMAN MELDRUM. Ahmedabad, India. *J. Chem. Soc.* 119, 201-9 (1921); cf. *C. A.* 14, 3401.—The condensation with gallic acid was undertaken as a possible means of ultimately obtaining 3,4,5-trihydroxyphthalic acid. 24 g. gallic acid, 10 g.  $\text{CCl}_3\text{CH}(\text{OH})_2$  and 100 cc. 94%  $\text{H}_2\text{SO}_4$  mixed and allowed to stand 48 hrs., gave 3,4,5-trihydroxy-2-trichloromethylphthalide,  $\text{C}_8\text{H}_5\text{O}_4\text{Cl}_3$ , double pyramids from acetone and  $\text{CHCl}_3$ ,  $m. 210-2^\circ$ . Triacetate, lustrous, silky needles from alc.,  $m. 172^\circ$ . Hydrolysis of these substances did not lead to definite results. When 24 g. gallic acid, 40 g.  $\text{CCl}_3\text{CH}(\text{OH})_2$  and 200 cc.  $\text{H}_2\text{SO}_4$  are allowed to stand 24 hrs., the lactone of 7,8-dihydroxy-2,4-bistrichloromethyl-6- $\beta$ -trichloro- $\alpha$ -hydroxyethyl-1,3-benzodioxine-5-carboxylic acid (I) results,  $\text{C}_{12}\text{H}_5\text{O}_6\text{Cl}_3$ , transparent stout plates from MeOH or EtOH with alc. of crystn., decomp.  $277-9^\circ$ . Disodium compound, yellow. Dipotassium compound, yellow. Dimethoxy derivative,  $\text{C}_{14}\text{H}_9\text{O}_6\text{Cl}_3$ , by the action of  $\text{Me}_2\text{SO}_4$ , prismatic needles,  $m. 192-3^\circ$ . Diacetate,  $\text{C}_{17}\text{H}_9\text{O}_8\text{Cl}_3$ , clusters of prismatic needles,  $m. 217-9^\circ$ . Dibenzate,  $\text{C}_{27}\text{H}_{17}\text{O}_8\text{Cl}_3$ , slender, prismatic needles,  $m. 234-6^\circ$ . 20 g. gallic acid, 60 g.  $\text{CCl}_3\text{CH}(\text{OH})_2$  and 250 cc.  $\text{H}_2\text{SO}_4$  gave the lactone of 7,8- $[\beta, \beta$ -trichloroethylenedioxy]-2,4-bistrichloromethyl-6- $[\beta, \beta$ -trichloro- $\alpha$ -hydroxyethyl]-1,3-benzodioxine-5-carboxylic acid (II),  $\text{C}_{14}\text{H}_9\text{O}_6\text{Cl}_3$ , amorphous powder, insol. in most org. solvents,  $m. 268-70^\circ$ . 6-Methyl-2,4-bistrichloromethyl-1,3-benzodioxine-8-carboxylic acid





(A),  $C_{12}H_7O_4Cl_6$ , results from 20 g. *p*-cresotic acid, 40 g.  $CCl_3CH(OH)_2$  and 160 cc. concd.  $H_2SO_4$ , after standing 5 days, fine needles from acetone, m. 285-6° (decompn.). **Sodium salt.** When 2 g. A, 40 cc. glacial AcOH and 10 g. Zn dust are heated, *4-hydroxy-5,5,β,β-dichloroethyl-m-toluic acid*,  $C_{10}H_{14}O_4Cl_2$ , results, needle-shaped crystals, m. 205-7°. The **calcium salt**, slender, glistening needles, is characteristic: Fused with KOH, the toluic acid gives *6-hydroxy-5-carboxy-m-tolylacetic acid*, soft needles, m. 257° (decompn.). **Silver salt.** *o*-Cresotic acid (5 g.), 5 g.  $CCl_3CH(OH)_2$  and 60 cc.  $H_2SO_4$  gave *β,β,β-trichloro-4,4'-dihydroxy-α,α-di-m-tolyliethane-5,5'-dicarboxylic acid*,  $C_{18}H_{18}O_6Cl_3$ , microcryst. powder, m. 283-5° (decompn.). **Calcium salt.** C. J. Waser

**Substituted quaternary azonium compounds containing an asymmetric nitrogen atom.** IV. Additive compounds of thiocarbamide with azonium iodides. BAWA KARTAR SINGH and MIRI LAL. Govt. College, Lahore, India. *J. Chem. Soc.* 119, 210-1 (1921); cf. C. A. 15, 59.—The following addition products of thiocarbamide were prepd.: **Phenylmethylethylazonium iodide**,  $PhMeEt(NH_2)NI \cdot 2CH_3N_3S$ , fine silky needles, m. 192-3°. **Phenylbenzylmethylazonium iodide**,  $Ph(PhCH_2)Me(NH_2)NI \cdot 2CH_3N_3S$ , m. 211°. **Phenylbenzylpropylazonium iodide**, m. 180-1°. **Phenylbenzylallylazonium iodide**,  $Ph(PhCH_2)(C_4H_9)(NH_2)NI \cdot CH_3C_6H_5S$ , fine silky needles, m. 187-8°.  $PhMe_2(H_2N)NI$  and  $PhEt_2(H_2N)NI$  do not form addition products. These products were prepd. by heating a concd. alc. soln. of the components (excess of thiocarbamide). The soln. was cooled, filtered, and the filtrate pptd. with dry  $Et_2O$ . C. J. Waser

**Condensation of *p*-nitrobenzyl chloride with nitroso compounds.** A new mode of formation of *N*-oximino ethers. FRED BARROW and EVAN DALTON GRIFFITHS. Birbeck College. *J. Chem. Soc.* 119, 212-6 (1921).—It has been found that  $PhNO$  and the  $NO$  derivs. of mono- and dialkylanilines condense with  $p-NO_2C_6H_4CH_2Cl$  to form *p*-nitrobenzaloxime *N*-aryl ethers: **Phenyl**,  $O_2NC_6H_4CH:NPh:O$ , from 8.6 g.  $p-NO_2C_6H_4CH_2Cl$  and 5.4 g.  $PhNO$  in alc. treated with 4.2 g. KOH in MeOH. On addition of the alkali, the ether sepd. as a yellow powder, which forms slender, pale yellow leaflets from alc., m. 182°. Upon hydrolysis with concd. HCl, it yields  $p-NO_2C_6H_4CHO$  and  $p-ClC_6H_4NH_2$ . The compd. was also prepd. by condensing  $p-O_2NC_6H_4CHO$  and  $\beta-PhNHOH$ . ***p*-Dimethylaminophenyl**,  $O_2NC_6H_4CH:NOC_6H_4NMe_2$ , from 28.6 g.  $p-O_2NC_6H_4CH_2Cl$  and 25 g.  $p-Me_2NC_6H_4NO$  in alc. treated with 9.3 g. KOH in 66 cc. MeOH, chocolate-red needles from  $C_6H_5N-EtOH$ , m. 201°. The salts are yellow. ***p*-Diethylaminophenyl**,  $C_{17}H_{19}O_2N_3$ , large, lustrous bright crimson leaflets, m. 167°. ***p*-Dipropylaminophenyl**,  $C_{18}H_{21}O_2N_3$ , felted, slender, dark crimson needles, m. 135-8°. ***p*-Ethylaminophenyl**,  $C_{16}H_{19}O_2N_3$ , deep crimson needles from  $C_6H_6$ , m. 168°. ***p*-Nitrophenyl**,  $C_{12}H_9O_2N_3$ , pale yellow powder from alc., m. 186°. Attempts to condense  $p-NO_2C_6H_4CH_2Cl$  with nitrosoamines were unsuccessful. It has also been found that aromatic Cl ketones react with  $NO$  compds. C. J. West

**The oxidation of carbazole.** WILLIAM HENRY PERKIN, JR. and STANLEY HORWOOD TUCKER. Oxford. *J. Chem. Soc.* 119, 216-25 (1921).—By the action of  $KMnO_4$  on carbazole in boiling soln., 3 substances are produced: 2 cryst. isomeric bicarbazyls, m. 220-1° and 265°, and an amorphous substance. All 3 substances can be nitrated and brominated and react with  $Ac_2O$ . 100 g. carbazole in 700 g. boiling pure acetone are treated with 2 portions of 50 g.  $KMnO_4$ . The boiling is continued until the pink color is discharged. The  $MnO_2$  is extd. twice with 400 g. boiling acetone and the whole filtrate evapd., giving 110 g. oxidation product. Dissolved in  $C_6H_6$ , crystals of *bicarbazyl* (A) sep. (24 g.). The filtrate is mixed with 2 vols. acetone, from which the isomeric *bicarbazyl* (B) seps. The acetone is evapd. off the filtrate from *bicarbazyl* (B), and the liquor is treated with alc., which gives a pink flocculent material (C). *Bicarbazyl* (A),  $C_{16}H_{12}N_2$ , m. 220-1°, orthorhombic crystals, *m* (110), *p* (111); *a:b:c*:0.5766:1:0.7182. The soln. in acetone exhibits a pale violet fluorescence and the crystals have a steel-blue

tint. An acetate could not be prepd. Concd.  $\text{H}_2\text{SO}_4$  gives an emerald-green soln., which turns deep blue on addition of a drop of  $\text{HNO}_3$ . It does not yield a picrate. B, m.  $265^\circ$ , small bright crystals from acetone or  $\text{Ac}_2\text{O}$ , m.  $268^\circ$  ( $273^\circ$  cor.). The soln. in warm concd.  $\text{H}_2\text{SO}_4$  is dull green, but is unaffected by  $\text{HNO}_3$ . C could not be obtained cryst. The soln. in concd.  $\text{H}_2\text{SO}_4$  is green. It reacts violently with Br and readily with  $\text{HNO}_3$ .

C. J. WESS

**The spectrochemistry of benzene derivatives.** K. v. AUWERS. *Ann.* 422, 160-91 (1921).—I. Halogen compounds: (With ADELHEID FRÜHLING).—Earlier investigations (C. A. 7, 480) showed that Cl played, spectrochemically, the same role as an alkyl group. In extending the work to the aromatic series, in which 34 Cl derivs. were studied, the same conclusion is reached: Cl resembles the alkyl group in its spectrochem. behavior and does not possess an unsatd. character. The same is true of Br and I. *Ethyl o-chlorocinnamate*,  $b_{118}$   $160^\circ$ ,  $d_{4}^{21.1}$  1.1683. II. Phenols and phenol ethers. *Hemimellitanyl methyl ether* (2,3,4-trimethylphenyl methyl ether),  $\text{C}_{10}\text{H}_{14}\text{O}$ , b.  $226-7^\circ$ , glistening prisms, m.  $28-9^\circ$ . *Ethyl ether*, b.  $237-8^\circ$ . *Mesityl ethyl ether*, b.  $217^\circ$ . The differences in the exaltations of the isomeric phenols and their ethers are so small as to be of no practical value. It is true, however, that if the phenol ether has 2 *o*-substituents, the values are considerably lower, and with the exception of the density, may be used to distinguish these compds. III. Amines. The 4 xylydines are investigated, but the observations must be extended to other compds. before conclusions can be drawn. The left-hand table shows the effects of various substituents upon the depression of the  $\text{C}_6\text{H}_6$  mol.; they are arranged in order of increasing exaltation. The right-hand table shows the effect of various substituents upon the sp. exaltation of an *o*-substituted alkali benzoate ( $\text{X} = \text{C}_6\text{H}_4\text{CO}_2\text{R}$ ):

Formula.	$\frac{\Delta}{\text{H}_2}$	$\frac{\Delta}{\text{H}_2}$	$\frac{\Delta}{\text{H}_2}$ %	$\frac{\Delta}{\text{H}_2}$ %	Formula.	$\frac{\Delta}{\text{H}_2}$	$\frac{\Delta}{\text{H}_2}$	$\frac{\Delta}{\text{H}_2}$ %	$\frac{\Delta}{\text{H}_2}$ %
$\text{C}_6\text{H}_6$ .....	-0.19	-0.22	8	7	XH.....	0.43	0.49	26	26
PhCl.....	-0.08	-0.09	9	10	XBr.....	0.31	0.31	20	21
PhBr.....	-0.03	-0.03	9	11	XCl.....	0.35	0.35	22	23
PhI.....	0.03	0.03	9	10	XMe.....	0.49	0.53	27	30
PhOH.....	0.12	0.13	13	18	XCOEt.....	0.53	0.55	26	29
PhAlk.....	0.18	0.17	11	12	XCO <sub>2</sub> Et.....	0.56	0.58	23	28
PhOAlk.....	0.35	0.35	19	21	XOMe.....	0.69	0.73	37	42
PhCO <sub>2</sub> Alk..	0.43	0.49	26	26	XCHO.....	0.75	0.77	37	41
PhC(:O)Alk.	0.51	0.57	31	33	XOH.....	0.84	0.90	56	64
PhNH <sub>2</sub> .....	0.87	0.92	35	41	XNH <sub>2</sub> .....	1.73	..	..	..
PhCHO.....	0.99	1.02	45	49					
PhCH:CH <sub>2</sub> ..	1.10	1.13	45	45					

C. J. WESS

**Constituents of resins.** VII. Lubanyl benzoate from Siamese benzoin. I. ALOIS ZINKE AND JOHANNA DZIRIMAL. *Monatsh.* 41, 423-41 (1921); cf. C. A. 15, 1016. —Lubanyl benzoate, prepd. according to Reinitzer (C. A. 9, 121), and purified by crystn. from  $\text{Et}_2\text{O}$ -petr. ether, m.  $72^\circ$ , has the formula  $\text{C}_{17}\text{H}_{16}\text{O}_4$  (3,4-MeO(HO) $\text{C}_6\text{H}_4\text{CH}:\text{CHCH}_2\text{O}(\text{Bz})?$ ). *Dibromide*, rose-colored needles, m.  $119-20^\circ$ ; cold concd.  $\text{H}_2\text{SO}_4$  gives a yellow color, which changes to violet on heating and then to blue. *Dibenzoate*, from the benzoate and  $\text{BzCl}$  with alkali, needles, m.  $79-80^\circ$ . It gives no reaction with  $\text{FeCl}_3$  (the dibromide gives a green color). *Dibenzoate dibromide*, needles, m.  $153-4^\circ$ . A consideration of the groups (Bz, MeO and OH) present led to the supposition that

lubanyl was coniferyl alc. This was confirmed in part by its behavior on hydrolysis, since it yields only amorphous substances. The 1st product is light brown, analyzes for  $C_{10}H_{12}O_4$  and m. 110–20°. Boiled with dil. AcOH it seems to polymerize to a brown amorphous mass, m. 217° (decompu.) and analyzes for  $C_{10}H_{12}O_4$  or  $C_{10}H_{12}O_6$ . Both products, heated with dil.  $H_2SO_4$  and Zn, gave eugenol. A preliminary oxidation expt. with HgO seemed to indicate the presence of vanillin and its acid in the oxidation products. The crystallographic properties of *d*-siaresinolic acid-acetic acid, the acid  $C_{27}H_{40}O_4$  from *d*-siaresinolic acid, and the acid  $C_{27}H_{40}O_4$  from *d*-sumaresinolic acid are given in detail.

C. J. WEST

**Action of hydrazine on chloral hydrate.** GUSTAV KNÖPPER. Brunn. *Monatsh.* 41, 455–66(1920); cf. C. A. 7, 2542.—3.5 g.  $C_3H_7ON_2Cl_2$  (from benzalazine and  $CCl_3CH(OH)_2$ ) in dil. KOH are treated with 9 g. cryst.  $FeSO_4$ , giving the compound  $C_3H_7ON_2Cl_2$ . The reaction is a combination of the splitting off of HCl and the addition of  $H_2$ . The same compd. is obtained by the action of  $(NH_2)_2.H_2O$  in AcOH. It forms fine, asbestos-like needles, m. 217°. The action of  $FeSO_4$  on  $C_3H_7ON_2Br_2$  gave  $C_3H_7ON_2Br_2$  (C. A. 11, 335). Cuminalazine and  $CCl_3CH(OH)_2$  give the compound  $C_{10}H_{13}ON_2Cl_2$ , m. 144°. Heated gently with KOH, it loses HCl, forming the compound  $C_{10}H_{13}ON_2Cl_2$ . Chloral semioxamazone,  $CCl_3CH:NNHCOCONH_2$ , from 4 g.  $H_2NNHCOCONH_2$  and 5.5 g.  $CCl_3CHO$ , m. 227° (decompu.). Chloralacetone hydrazone,  $CCl_3CH(OH)NHN:CM_2$ , from  $CCl_3CH(OH)_2$  and  $Me_2C:NN:CM_2$ , m. 91°; the compd. decomps. in 2–3 days; acids decomp. it, forming a brown soln. KOH splits off  $CHCl_3$ . Bromalacetone hydrazone,  $C_6H_5ON_2Br_2$ , m. 80°. Chloralmethylethyl ketone hydrazone,  $C_6H_5ON_2Cl_2$ , from  $CCl_3CH(OH)_2$  and  $MeEtCN:NMeEt$ , m. 97°. Bromalmethylethyl ketone hydrazone,  $C_6H_5ON_2Br_2$ , m. 80–1°.

C. J. WEST

**sym-Bromobenzenedisulfonic acid.** S. C. J. OLIVIER AND K. J. B. DE KLEER-MAEKER, Jr. Univ. d'Agric., Wageningen. *Rec. trav. chim.* 39, 640–5(1920).—Recently O. showed that the *sym*-acid is formed when the 2nd  $SO_3H$  group is introduced into *p*- $ClC_6H_4SO_3H$  at 300° (C. A. 14, 2470, 2471). It appeared that the same change might occur with *p*- $BrC_6H_4SO_3H$ . Herzig (*Monatsh.* 2, 192(1881)) obtained 2 isomers, one of which might have been the *sym*- $BrC_6H_4(SO_3H)_2$ . This sulfonation was repeated by a method previously used (C. A. 13, 2341). *p*- $BrC_6H_4SO_3H$  mixed with  $H_2SO_4$  in the ratio of 1:10 was boiled under a condenser for 8 hrs., cooled, poured into  $H_2O$  and converted into the Pb salt. In this way a 40% yield of the crude product was obtained. This was fractionally crystd. and the fractions were converted into the K salt and then into the sulfonyl chloride with  $PCl_5$ . Only one sulfonyl chloride,  $C_6H_4Br(SO_2Cl)_2$ , m. 99–100°, was isolated and analyzed. The 1st fraction gave a little material which contained less Cl than  $C_6H_4Br(SO_2Cl)_2$  but which was not identified. The diamide was obtained as needles, m. 255–6°, by treating the chloride with concd.  $NH_4OH$ . The barium salt  $C_6H_4Br(SO_3)_2Ba.2.5H_2O$  was obtained from both the chloride and the sulfonation product direct by. The potassium salt also is described. The  $C_6H_4Br(SO_2Cl)_2$  heated with 8 g.  $PCl_5$  in a sealed tube at 230–40° for 6 hrs. gave 0.050 g. *sym*- $C_6H_4Cl_2$ , m. 63°. Because of the difficulty of the above reaction the constitution was proved by the following process:  $BrC_6H_4(SO_3H)_2 \rightarrow H_2NC_6H_4(SO_2NH_2)_2 \rightarrow H_2NC_6H_4(SO_3H)_2 \rightarrow N:N.C_6H_4(SO_3H)_2 \rightarrow ClC_6H_4(SO_3H)_2 \rightarrow ClC_6H_4(SO_2Cl)_2$ , the details of which are

given. The paper concludes with a summarized statement of the wrong data given in Beilstein and Richter concerning the bromobenzenedisulfonic acids.

E. J. WITZEMANN

**Solubility of milk sugar.** J. GILLIS. Gand. *Rec. trav. chim.* 39, 677–8(1920).—Recently G. published (C. A. 14, 2472) the soly. curve of lactose at temps. above 90°. These data, together with those of Hudson (C. A. 3, 272), for temps. below 80°,

permit of designating 93.5° as the transi-dehydration point for  $\alpha$ -lactose.  $\text{H}_2\text{O} \rightleftharpoons \beta$ -lactose +  $\text{H}_2\text{O}$ . Soly. detns. of Saillard (C. A. 14, 873) deviate from those of H., especially near 65°, where they differ 3%. Moreover, the soly. at 89° detd. by H. differs from that of G. (l. c.). G. has repeated these detns. by his method of watching for the disappearance of the last crystal and gives numerical results in a table. E. J. WITZEMANN

The sensitiveness of hexanitrodiphenyl to mechanical influences compared with that of hexanitro compounds of analogous constitution. C. F. VAN DUIN. Utrecht. *Rec. trav. chim.* 39, 685-8(1920).—In a preceding paper v. D. and Brackmann (C. A. 13, 1638) showed that the use of trinitrophenylmethylnitroamine (A) is often limited by its sensitiveness to mechanical influences. Some hexa- $\text{NO}_2$  derivs. of 2-ring compds. have been recommended (v. D. and v. Lennep, C. A. 14, 2471, 2708), but recent work (v. D. and v. L., C. A. 14, 2708) has shown that the mechanical sensitiveness of these is greater than that of A. Ullmann and Bielecki (Ber. 34, 2179(1901)), who first prepd. hexanitrodiphenyl (C) said that it is mechanically stable but this seemed improbable when the sensitiveness of *sym*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$  (B) is considered. In compds. of analogous constitution the sensitiveness increases with the heat of explosion. Muraour (C. A. 13, 1766) has confirmed the opinion that the rule of Mallard and LeChatelier (*Mém. des poudres et salpêtres* II, 445, 474(1884-9)) may be applied and according to this rule B should be a little more sensitive mechanically than C. The method of U. and B. was used to prep. B: 15 g. "Naturkupfer C" were added to 20 g. picryl chloride in 200 cc.  $\text{PhNO}_2$  at 160-80°, kept at this temp. 15 mins. with agitation, freed from the  $\text{PhNO}_2$  by steam distn., and extd. with boiling EtOH to remove unchanged picryl chloride. The residue B when crystd. from glacial AcOH m. 242° without decompn. With the method previously described (C. A. 14, 2708) and a 10 kg. wt., the results showed that B is more sensitive to mechanical influences than C but is also much less sensitive than A. E. J. WITZEMANN

$\alpha$ -Sulfopropionic acid and its acid salts. A. P. N. FRANCHIMONT AND H. J. BACKER. Univ. Leyden and Groningen. *Rec. trav. chim.* 39, 689-93(1920).— $\alpha$ -Sulfopropionic acid (A) is extremely hygroscopic, crysts. with 1 mol.  $\text{H}_2\text{O}$ , m. 100.5°. The formation of acid salts is of interest because of the 2 different acid functions. Neutral salts of A have been known but until now not acid salts. The free acid is a strong acid but the acid salts are feeble org. acids showing that the 2 acid functions differ considerably in strength. This acidity of the acid salts is due to the  $\text{CO}_2\text{H}$ , the acidity of which is apparently not increased by the introduction of the  $\text{SO}_3\text{H}$  group. The acid salt of strychnine is an excellent sample to illustrate the theory of indicators. Its acid character is such that a small amt. of base makes it turn Me orange. But if litmus or Me red is used the acid salt requires 1 equiv. of base. With phenolphthalein 2 equivs. of base are required, since the color does not change until all strychnine is liberated. A was at first prepd. from  $\text{H}_2\text{SO}_4$  and  $(\text{EtCO})_2\text{O}$  but other methods were used later (Backer Dubsky, C. A. 15, 1508). The acid was purified by crystn. from  $\text{H}_2\text{O}$  as the Ba salt, from which the free acid was liberated with the mol. amt. of  $\text{H}_2\text{SO}_4$ . The concd. aq. soln. was evapd. in a desiccator but shows no tendency to cryst. until placed in the cold for some time. The acid potassium salt  $\text{MeCH}(\text{CO}_2\text{H})\text{SO}_3\text{K}$ , the acid barium salt, the acid aniline salt, white needles, m.  $\approx 163^\circ$ , the acid  $\alpha$ -naphthylamine salt, bluish spangles, soften  $\approx 228^\circ$ , m. 233°, and the acid strychnine salt were prepd. and analyzed. E. J. WITZEMANN

Crystallized acetylphenylurethan. D. R. NIJK. Univ. Leyden. *Rec. trav. chim.* 39, 699-703(1920).—Acetylphenylurethan (A),  $\text{PhNAcCO}_2\text{Et}$ , can be prepd. from  $\text{PhNH}_2$  (1) by introducing the Ac group first and then the  $\text{CO}_2\text{Et}$  and (2) by introducing the  $\text{CO}_2\text{Et}$  first and then the Ac group. N. has obtained  $\text{PhAcNCO}_2\text{Et}$  from  $\text{PhAcNNa} + \text{ClCO}_2\text{Et}$  instead of A, which N. confirmed and found to be due to substitution of Ac by

$\text{CO}_2\text{Et}$ . 30 g.  $\text{PhNHAc}$  in excess of  $\text{C}_6\text{H}_6$  was warmed with 5.1 g. Na wire until dissolved. The calcd. amt. of  $\text{ClCO}_2\text{Et}$  in 25 g.  $\text{C}_6\text{H}_6$  was added slowly at room temp. After cooling some time 2 layers were formed. On heating the  $\text{C}_6\text{H}_6$  was evapd. and finally A was removed from the NaCl by distg. *in vacuo*. 40 g. A was obtained as a thick oil,  $b_7$  171°,  $b_{10}$  142°. A was crystd. by placing in a liquid-air bath, after trying other cooling mixts. in vain. The mass obtained was pressed out on a suction filter and from petroleum ether gave well formed crystals, m. 59°. Sanders (*J. Am. Chem. Soc.* 22, 378(1900)) obtained A as a thick oil on acetylating  $\text{PhNHCO}_2\text{Et}$  with  $\text{Ac}_2\text{O}$  and  $\text{AcCl}$ . N. boiled 10 g.  $\text{PhNHCO}_2\text{Et}$  with 10 g.  $\text{Ac}_2\text{O}$  and 2 g.  $\text{AcCl}$  for 2 hrs. After distg. *in vacuo* A was obtained as a solid which crystals in petr. ether and m. 59°. The crystallographic description is given in full: bipyramidal rhombs.,  $a:b:c = 1.2323:1:1.5141$ . 3 g.  $p\text{-H}_2\text{NC}_6\text{H}_4\text{COMe} + 3$  g. powdered KOH in 30 cc. dry EtOH were heated under a reflux condenser and treated with 2.4 g.  $\text{ClCO}_2\text{Et}$  in 30 cc.  $\text{Et}_2\text{O}$ . The mixt. was heated 1 hr. and the  $p$ -acetophenylurethan sepd.; colorless crystals from  $\text{EtOH}$ , m. 158°.

E. J. WITZEMANN

The action of sodium hypochlorite on the acid amides. II. I. J. RINKES. Rijkszuivelschool, Bolsward. *Rec. trav. chim.* 39, 704-10(1920).—In continuing his previous work (cf. C. A. 14, 2474), R. has used phenylpropionic amide (A),  $\text{PhC}:\text{C}(\text{NH}_2)\text{CO}_2\text{H}$ . As in previous expts. A was heated in MeOH with NaOCl but failed to give a cryst. urethan; it gave  $\text{PhCH}_2\text{CN}$  (B),  $b_7$  233.5°, m. -23.1°, instead. No intermediate product was obtained. Finely powdered A treated with NaOCl soln. in an ice bath and then with 5% AcOH sepd. chlorophenylpropionic amide,  $\text{PhC}:\text{C}(\text{NH}_2)\text{CO}_2\text{H}$  which, with the calcd. amt. of  $\text{Ba}(\text{OH})_2$ , was converted into the barium phenylacetylenecarboximate (C),  $(\text{PhC}:\text{CNHCO}_2)_2\text{Ba}$ , nearly colorless crystals. On passing steam through the solns. of C  $\text{BaCO}_3$  is pptd. and B is volatilized.  $\text{PhC}:\text{CNH}_2$ , which should be an intermediate in this process, is transformed into B. C moistened with dil. HCl gives  $\text{CO}_2$ ,  $\text{BaCl}_2$  and B. The transformation of A in  $\text{H}_2\text{O}$ -MeOH by NaOCl may be explained in the same way as the transformation of C by  $\text{Ba}(\text{OH})_2$ . No indications of the formation of a urethan were obtained with A. By the use of NaOCl R. has obtained  $\alpha$ -hydroxyphenylacetaldehyde (D) (*dl*-mandelic aldehyde), which Nef (*Ann.* 335, 268(1904)) and Evans (*Am. Chem. J.* 35, 115(1906)) said is at once transformed into  $\text{BzCH}_2\text{OH}$ .  $\text{PhCH}:\text{CHCONH}_2$  was converted into styrylurethan with NaOCl in  $\text{MeOH}$ - $\text{H}_2\text{O}$ . This treated with the calcd. amt. of  $\text{KMnO}_4$  in  $\text{Me}_2\text{CO}$  at low temps. gave dihydroxydihydrostyrylmethane,  $\text{PhCH}(\text{OH})\text{CH}(\text{OH})\text{NHCO}_2\text{Me}$ , which by decomp. with 1.0 N  $\text{H}_2\text{SO}_4$  and distn. with steam gave D as a colorless oil.

E. J. WITZEMANN

Constitution and synthesis of meconic acid. H. THOMS AND PIETRULLA. Univ. Berlin. *Pharm. Monatshefte* 1, 148-7(1920).—An address descriptive of apparently successful expts. leading to the conversion of Etacetonedioxalate into meconic acid, and showing this acid to be a pyrone deriv., *i. e.*, a di- $\text{CO}_2\text{H}$  acid of hydroxypyrrone.

W. O. E.

A new hydroxystearic acid from reduced castor oil. H. THOMS AND W. DRCKERY. Univ. Berlin. *Pharm. Monatshefte* 1, 147(1920).—An address descriptive of the hydroxystearic acid,  $\text{Me}(\text{CH}_2)_8\text{CH}(\text{OH})(\text{CH}_2)_{10}\text{CO}_2\text{H}$ , isolated from a com. fat (hardened castor oil), m. 83°. Dehydration with 60%  $\text{H}_2\text{SO}_4$  led to the formation of a mixt. of oleic acids; this on oxidation with  $\text{KMnO}_4$  yielded an acid mixt., from which after esterification capronic, enanthic and decamethylenedicarboxylic acids were isolated.

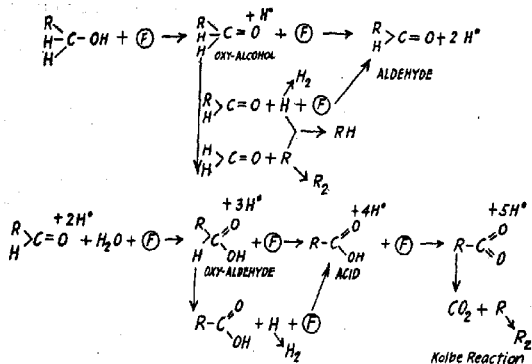
W. O. E.

The picrates of the nitrogen bases of the alcohol radicals. A. RIGGS. Bamberg. *Z. Kryst. Min.* 55, 454-522(1920).—Complete crystallographic descriptions and transition data are given for the following substituted ammonium picrates: Me, trimorphous, at low temps. rhombic sphenoidal, above 58° passes into rhombic holo-

hedral and above  $63^\circ$  into a 3rd form; 7 Et, monoclinic at ordinary temps., with a higher and a lower temp. form; 2-Pr, monoclinic-domatic; *iso*-Pr, triclinic; *n*-Bu and *iso*-Bu, triclinic; Am, triclinic; heptyl, monoclinic. The secondary amines: Me<sub>2</sub>, 2 rhombic forms; MeEt, a triclinic and 2 rhombic forms; Pr<sub>2</sub>, monoclinic-sphenoidal the Tertiary amines: Me<sub>3</sub>, 2 monoclinic and a 3rd form of undetd. crystn.; Me<sub>2</sub>Et, 1 monoclinic domatic and 2 rhombic forms; MeEt<sub>2</sub>, 2 forms, monoclinic; Et<sub>3</sub>, 1 rhombic, and 2 other forms. Quaternary amines: Me<sub>4</sub>, 1st triclinic-asymmetric, 2nd pseudo-hexagonal, and 3rd hexagonal; Me<sub>2</sub>Et, hexagonal; Me<sub>2</sub>Et<sub>2</sub>, hexagonal; MeEt<sub>3</sub>, 1 monoclinic and 2 hexagonal forms; Me<sub>3</sub>Pr, 1st triclinic, 2nd pseudo-hexagonal and 3rd hexagonal; Me<sub>3</sub>(*iso*-Pr), hexagonal; Me<sub>3</sub>Bu, 1st monoclinic, 2nd triclinic and 3rd and 4th forms hexagonal; Me<sub>4</sub>(*iso*-Bu), remarkable in showing 5 polymorphs, 1st monoclinic, 2nd triclinic, 3rd monoclinic-domatic, 4th triclinic-asymmetric, and 5th hexagonal; Et<sub>4</sub>, 1st monoclinic, 2nd hexagonal; Me<sub>2</sub>Pr<sub>2</sub>, 1st triclinic and 2nd hexagonal; Et<sub>2</sub>Pr, 1st monoclinic, 2nd of undetd. crystn., 3rd hexagonal; MeEt<sub>2</sub>Pr<sub>2</sub>, 1st triclinic-asymmetric, 2nd hexagonal; Et<sub>2</sub>Pr<sub>2</sub>, 1st monoclinic-domatic, 2 others of undetd. crystn.; Me<sub>3</sub>Pr, 1st monoclinic, 2nd undetd.; Et<sub>4</sub>Pr, triclinic; and Pr<sub>4</sub>, 1st monoclinic and 2nd undetd.

E. T. WHERRY

**Electrolytic oxidation of methanol and of ethyl alcohol in alkaline solution. Electrolytic formation of methane.** ERICH MÜLLER AND ANTONIO R. Y. MIRO. Dresden. *Z. Elektrochem.* 27, 54-7(1921).—During the electrolytic oxidation of MeOH at Pt

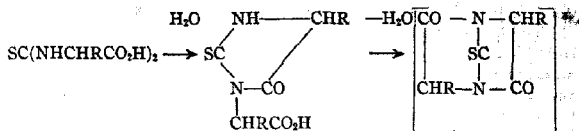


anodes in alk. soln., small quantities of H are formed; while with EtOH both H and CH<sub>4</sub> result. The following scheme is suggested as representing the various stages in the electrolytic oxidation of MeOH and EtOH:

H. J. CREIGHTON

**Thiocarbimide reaction.** I. SHINTARO KODAMA. *J. Tokyo Chem. Soc.* 41, 951-65(1920).—Thiocarbimide reactions of various substances are first reviewed and discussed. Then the reaction between CS<sub>2</sub> and NH<sub>2</sub> acids is studied. An attempt to convert leucine, phenylalanine, and tyrosine to *sym*-thiocarbonylbisamino acids and then to thiocarbimides was not successful. In the presence of NaHCO<sub>3</sub>, however, the condensation takes place easily, the fact suggesting that the NH<sub>2</sub> acids must be in the form of their internal salts. The condensation product, the Na salt of the corresponding  $\alpha$ -thiocarbonyl-*sym*-bisamino acid, can easily be converted to the acid by addition of an acid. These  $\alpha$ -thiocarbonyl-*sym*-bisamino acids, however, when heated with

alc. HCl, instead of giving thiocarbimide acid, produce thiohydantoin, the reaction probably proceeding according to the scheme:



Glycine, Na glutamate, and histidine monochloride do not undergo a similar reaction as do the above  $\text{NH}_2$  acids. These acids, during condensation with  $\text{CS}_2$ , split off the theoretical amt. of  $\text{H}_2\text{S}$ ; the fact may be of great value for extn. of  $\text{NH}_2$  acids in contrast with Van Slyke's method. S. T.

**Odor of apples; etheral oils obtained from leucic acid.** SHINTARO KODAMA. *J. Tokyo Chem. Soc.* 41, 965-74(1920).—A method of manuf. from by-products of the amino acid industry of the active principle of the aromatic odor of apples, such as Am esters of fatty acids, is proposed. For making amyl valerate, isovaleraldehyde is prepd. from anhydrous leucic acid obtained from leucine. The aldehyde can easily be purified by  $\text{NaHSO}_3$ , and subsequent decompn. with  $\text{H}_2\text{SO}_4$ . Al amyloxyde converts the aldehyde into amyl valerate. Isocaproic ester is prepd. by reduction of  $\alpha$ -chloroisocaproic acid, produced by treatment of leucic ester with HCl and  $\text{NaNO}_2$ . Various other etheral oils are prepd. from leucic acid and their properties recorded. I.  $\text{Me}_3\text{CHCH}_2\text{CH}(\text{OAc})\text{CO}_2\text{Et}$ . Leucic acid ester is prepd. by treating leucic acid (m.  $75^\circ$ ), with alc.  $\text{H}_2\text{SO}_4$ . It  $b_{18-20}$   $87-9.5^\circ$ , has a sweet odor. 5 g. of this ester and 5 g.  $\text{AcCl}$  are heated for 4 hrs. and distd. from a slightly alk. soln. The distillate  $b_{18}$   $120-1^\circ$ , is colorless and has an odor like soy sauce. In alc. soln.,  $[\alpha]_D^{22}$   $-29.4^\circ$ . II.  $\text{Me}_3\text{CHCH}_2\text{CH}(\text{OAc})\text{CO}_2\text{Me}$  is obtained by acetylating Me leucate ( $b_{18-20}$   $80-2^\circ$ ). It  $b_{18}$   $99-100$ , smells like I. III.  $\text{Me}_3\text{CHCH}_2\text{CH}(\text{OBz})\text{CO}_2\text{Et}$  is prepd. by heating Et leucate with  $\text{BzCl}$ . It  $b_{17}$   $174-6^\circ$ , is colorless, has a turpentine-like odor. IV.  $\text{Me}_3\text{CHCH}_2\text{CH}(\text{OCOC}_6\text{H}_5)\text{CO}_2\text{Et}$ ,  $b_{18}$   $125-8^\circ$ , with a peppermint-like odor, is prepd. by heating the ester with isovaleryl chloride. V.  $\text{Me}_3\text{CHCH}_2\text{CH}(\text{CO}_2\text{Et})\text{OCOCHClCH}_2\text{CHMe}_2$ ,  $b_{18}$   $152-3^\circ$ , burning odor, is prepd. by treating the ester with  $\alpha$ -chloroisocapronyl chloride. VI.  $\text{Me}_3\text{CHCH}_2\text{CHClCO}_2\text{C}_6\text{H}_{11}$ , prepd. by treating the ester with  $\alpha$ -chloroisocapronyl chloride and  $\text{AmOH}$ ,  $b_{18-16}$   $113-4^\circ$ , is colorless, and has a stale orange odor. When reduced with  $\text{NaHg}$ , Et amylisocapronate is produced, which has a typical apple odor. VII. The methods of prepn. of  $\text{Me}_3\text{CHCH}_2\text{CH}(\text{OAc})\text{CCl:NPh}$  and  $\text{Me}_3\text{CHCH}_2\text{CH}(\text{OEt})\text{CHO}$  also are given. S. T.

**The chemical structure of chondridin.** P. A. LEVENE AND J. LOPEZ-SUAREZ. Rockefeller Inst. *J. Biol. Chem.* 45, 467-71(1921).—The ehondridin of Hebbing (C. A. 8, 3429) appears to be a lactone of chondrosin, crystg. with 2.5  $\text{H}_2\text{O}$ . The substance is neutral but on standing overnight with excess  $\text{NaOH}$ , 0.1 g. neutralized 2.55 cc. 0.1  $N$  alkali, indicating a mol. wt. of 392. It loses 1.5  $\text{H}_2\text{O}$  at  $100^\circ$  and reduced pressure.  $[\alpha]_D^{20}$   $60.6^\circ$ . C, H and N detns. agreed with the calcd. values. Glucuronic acid (furfural phloroglucide method), found 37.2%; calcd. 50.77%. I. GREENWALD

**A possible asymmetry of aliphatic diazo compounds.** P. A. LEVENE AND L. A. MIKESKA. Rockefeller Inst. *J. Biol. Chem.* 45, 593-4(1921); cf. Levene, and La Forge (C. A. 9, 2078; 13, 1215) and Marvel and Noyes (C. A. 15, 527).—*D*-Aspartic acid was converted into Et diazosuccinate. This was distd. under 0.08-0.12 mm.  $[\alpha]_D^{20}$  varied, in different prepn., from  $0.85^\circ$  to  $1.34^\circ$ . I. GREENWALD

**Manufacture of *m*-phenylenediamine.** H. M. GRENSEL. *Color Trade J.* 8, 21-2 (1921).— $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$  is prepd. on the com. scale by reducing  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$  with Fe borings, water and small amts. of HCl at 95-97°. Completeness of reduction is tested by spotting on filter-paper. Hints are given as to points to be observed in the construction of the app. used. Stress is laid on complete extn. of Fe sludges by hot  $\text{H}_2\text{O}$ , to avoid loss of product (8-10% sometimes remains in the sludge, if it is not thoroughly extd.).

F. S. BRATTIE

**Preparation of some hydrazines.** LEONARD THOMPSON. *J. Soc. Dyers and Colourists* 37, 7-11 (1921).—Fischer's method consists in the conversion of a diazotized amine to the diazosulfonic acid by treatment with  $\text{Na}_2\text{SO}_3$ , reduction of this to the corresponding hydrazinesulfonic acid by treatment with Zn dust and AcOH, and splitting off the sulfonic acid group by boiling with HCl. Meyer's method, in which the diazotized amine is directly reduced to the hydrazine by use of  $\text{SnCl}_2$  and HCl, is compared with the former method.  $\text{PhNHNH}_2$ , its *p*-sulfonic acid, and its *p*- and *m*- $\text{NO}_2$  substitution products, are mentioned in this connection. The above direct reduction of the diazotized amine to a hydrazine can be carried out by the use of  $\text{Na}_2\text{S}_2\text{O}_4$ , more simply than by the preceding methods, and with better yields. The following examples are given: *Phenylhydrazine*.—18.6 g.  $\text{PhNH}_2$  in 55 cc. HCl and 50 g. ice are diazotized with 15 g.  $\text{NaNO}_2$  in 30 cc.  $\text{H}_2\text{O}$  at 0°, the clear diazo soln. mixed with 20 cc. HCl, and a cold soln. of 46 g.  $\text{Na}_2\text{S}_2\text{O}_4$  (80%) in 250 cc.  $\text{H}_2\text{O}$  + a few drops of NaOH soln. added fairly rapidly and with stirring. 100 cc. HCl are then added, and the mixt. is boiled for a few min. The soln. on cooling, deposits the HCl salt of the product in a yield of 24.5 g. or 85% of theory, a further 7% being obtainable from the liquor. The yield by this method exceeds that from the other methods. *Phenylhydrazine-p-sulfonic acid*.—19 g. crystd. sulfanilic acid are dissolved in 23 cc. of 20% NaOH + 100 cc.  $\text{H}_2\text{O}$ . 7 g.  $\text{NaNO}_2$  are dissolved in this, and the mixt. is poured into a cold soln. of 12 cc.  $\text{H}_2\text{SO}_4$  in 100 cc.  $\text{H}_2\text{O}$ . The pptd. diazo compd. is filtered off, stirred to a paste with  $\text{H}_2\text{O}$ , and reduced with a cold soln. of 22 g.  $\text{Na}_2\text{S}_2\text{O}_4$  in 125 cc.  $\text{H}_2\text{O}$ , 20 cc. HCl being added during the reduction. 30 cc. HCl are then added and the soln. is boiled down to crystn.; the free base is obtained in this case, in a yield of 60%. *p-Nitro-phenylhydrazine*.—Reduction of  $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2\text{Cl}$  with  $\text{Na}_2\text{S}_2\text{O}_4$  does not give good results by this method. The nitrosamine compd. produced by pouring the diazo solution into NaOH (*Ber.* 27, 514), gives the desired product as follows: 10 g. of it are mixed with a little  $\text{H}_2\text{O}$  containing 6 g. NaOH, and reduced at 0° with 20 g.  $\text{Na}_2\text{S}_2\text{O}_4$  in 120 cc.  $\text{H}_2\text{O}$ . 200 cc. HCl are then added, and the soln. is boiled for a short time. The cooled soln., neutralized with  $\text{Na}_2\text{CO}_3$  and NaOAc, gives 6.2 g. of the free base directly, and a further 0.8 g. by extn. with  $\text{H}_2\text{O}$ . Yield, 95% of theory. The prepn. of *m-nitrophenylhydrazine* by this method has not been successful.  $\text{TiCl}_3$  succeeds here to a certain extent, but is of little practical value. Reference is made to a possible bearing of the subject upon the production of white resists under insol. azo colors in calico printing. "Nascent" hyposulfite (a mixt. of  $\text{NaHSO}_3$  lye and Zn-dust) cannot be used in place of  $\text{Na}_2\text{S}_2\text{O}_4$ . Mention is further made of the value of  $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHNH}_2$  as a delicate qual. test for *oxy-cellulose* in fabrics (deep orange stain fairly fast to washing).

F. S. BRATTIE

**The manufacture of acetic anhydride.** R. PORTER. *Chem. Trade J.* 68, 206 (1921).—The NaOAc used should contain not more than 0.10%  $\text{H}_2\text{O}$  or 0.05% alkali; the  $\text{S}_2\text{Cl}_2$  should be amber-colored and of high quality. The "hot process" of manuf., which consists in adding  $\text{S}_2\text{Cl}_2$  to the hot finely ground NaOAc at a definite rate, if carefully controlled will give very good results and is more dependable than the "cold process" which gives a higher yield but takes a much longer time to complete. In the

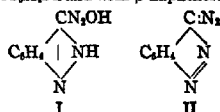


'cold process' the  $S_2Cl_2$  is added to a mixt. of  $NaOAc$  and  $Ac_2O$ , which is cooled by circulating  $H_2O$  around the mixer. After the addition is complete the mass is kept cool for 1 hr., then heated with steam and finally distd. in vacuum. The best mixer for these processes is one of the ball mill type, which revolves on roller bearings and is steam-jacketed.  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Cl}$ , a solid by-product from saccharin manuf., may be substituted for  $S_2Cl_2$  but it is difficult to work with because it has to be fused before using and its m. p. is near its decompn. temp. The  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Na}$  formed in the reaction may be easily recovered.  $Ac_2O$  is purified by distn. in a vacuum of 25-30 in. in cast-Fe jacketed stills fitted with stirrers, condensing coils, receivers and piping of Al. The receivers and storage tanks for the pure  $Ac_2O$  should be of Al. The principal impurities are S, which is removed by putting  $CuO$  in the stills, and Cl compds., which are removed by stirring with anhydrous  $NaOAc$ . Good quality (85%)  $Ac_2O$  can be purified with a loss of 2-3%, and there is usually an increase of 1-3% in strength. G. W. SMATTON

**Supplementary remarks on nitrosophenylhydroxylamine, nitrosoacetanilides and "diaz anhydrides."** RUG. BAMBERGER. Eidgenöss. Polytech., Zürich. *Ber.* 53B, 2308-20(1920).—In 1894 B. obtained from "diazobenzene perbromide" and alkalis, besides  $PhNHNO_2$ , minute amts. of an acid (or pseudo acid) (*Ber.* 27, 1274, 1554(1894)), which he assumed (correctly, as shown later, *C. A.* 4, 183, to be the then unknown  $PhN(NO)OH$  because with acids it decompd. into  $PhNO$  and  $NOH$  (?)). At the time, owing to the universal acceptance of the Kekulé diazo formulas, B. wrongly interpreted the reaction, considering it a substitution process, not an oxidation of the phenyldiazotate. Even at the present day, when  $PhN(NO)OH$  and  $NOH$  have been known for a long time, the equation  $PhN(NO)OH = PhNO + NOH$  cannot be withdrawn from the realm of the hypothetical. It has neither been detd. how the radical  $NO$  is split off nor has the action of acids been sufficiently investigated in all directions. Beside  $PhNO_2$ , there were found considerable amts. of phenyldiazonium salt (*C. A.* 9, 1780), undoubtedly produced by the diazotizing action of the  $HNO_3$  (or  $NOH$ ) formed in the decompn. Köpcke (*Diss. Zurich*, 1899) found that when dry  $HCl$  is passed 1 hr. through 5 g.  $PhN(NO)OH$  in 100 cc. cold  $Et_2O$ , the soln. becomes green, then brown and deposits 5.3 g. of white crystals, easily sol. in a little  $H_2O$  and containing the diazonium salts of  $PhNH_2$  and  $2,4\text{-Cl}_2C_6H_3NH_2$ . The aq. soln. is poured into alk.  $\beta$ -naphthol and from the abundant ppt. of red dyes is isolated, by repeated crystn. from alc. and then from  $C_6H_6$ , pure  $\beta\text{-HOC}_6H_4N:NPh$ ; the mother liquors give, besides further amts. of the above dye, after systematic fractionation from  $C_6H_6$ ,  $AmOH$  and  $EtOH$ ,  $2,4\text{-Cl}_2C_6H_3N:NC_6H_4OH$ , red needles, m. 189-90°. The  $Et_2O$  filtrate from the diazonium salts, freed from the rest of these salts by shaking with ice  $H_2O$  and dried, yields 1.8 g. of a cryst. residue from which, by fractional distn. with steam, is obtained  $PhNO$ , m. 68° after crystn. from  $AcOH$ ; the following fractions possibly contain some azoxybenzene and the small resinous residue more of this compd. and  $(p\text{-ClC}_6H_4)_2N_2O$  (?). When the treatment with  $HCl$  was stopped after 25 min. instead of 1 hr. in order, if possible, to detect any  $PhNHOH$  formed as an intermediate product, and the white crystals in cold  $H_2O$  were treated with  $NaHCO_3$  and quickly extd. with  $Et_2O$ , the dried ext. yielded a few yellowish granules in which the presence of an arylhydroxylamine was distinctly indicated by the action of  $FeCl_3$  ( $PhNO$  odor) and of Fehling soln. ( $CuOH$ ). Under the above conditions, then, the  $PhNO_2$  is in part attacked by the  $HCl$ , forming  $2,4\text{-Cl}_2C_6H_3NH_2$ , which in turn undergoes diazotization. Similarly, from 5.1 g.  $p\text{-BrC}_6H_4N(NO)OH$  were obtained 4.9 g.  $\beta$ -naphthol dye, from which, after tedious crystns. from  $AmOH$ ,  $EtOH$  and xylene were isolated red prisms, m. 207°, of  $2,4\text{-ClBrC}_6H_3N:NC_6H_4OH$ ; the mother liquors yield  $p\text{-BrC}_6H_4N:NC_6H_4OH$ , m. 172° after crystn. from xylene, alc. and  $C_6H_6$ ; the residue (1.7 g.) left by the  $Et_2O$  soln. yields on fractional distn. with steam  $p\text{-BrC}_6H_4NO$  (identified by conversion with

$\text{PhNHNH}_2$  into  $\text{BrC}_6\text{H}_4\text{N}(\text{OH})\text{N}_2\text{Ph}$ , m.  $128.5^\circ$ ) and a small amt. of yellowish crystals, m.  $126^\circ$ , probably containing  $(p\text{-BrC}_6\text{H}_4)_2\text{N}_2\text{O}$ . As he has repeatedly stated, B. believes, in agreement with Angeli, that the nitrosamine itself has the structure  $\text{PhN}(\text{NO})\text{OH}$  while its salts and esters are probably derived from the isomeric form  $\text{PhN}(\text{:O})\text{NOH}$ . The possibility of a similar tautomerism was suggested in 1894 for nitrosoacetanilide ( $\text{PhN}(\text{NO})\text{Ac} \rightleftharpoons \text{PhN}:\text{NOAc}$ ) which "under the most varied conditions shows the behavior of a diazo compdc." (*Ber.* 30, 366 (1897) and earlier papers), although the reactions of the nitrosoanilides can be satisfactorily explained on the basis of the usual nitrosamine formula by the assumption of intermediate addition products. In view of the "diazo-like behavior" of these compds. the question arose whether by cautious sapon. with alkalis they might not be converted into those yellow, explosive and extraordinarily reactive "diazo anhydrides" which are formed by the decompn. of diazonium salts with  $\text{NaOH}$  or of normal (*syn*) diazotates with  $\text{AcOH}$  as the products of the spontaneous anhydridization of the intermediate diazo hydroxides; 0.67 g.  $p\text{-ClC}_6\text{H}_4\text{N}(\text{NO})\text{Ac}$  in 25 cc.  $\text{Me}_2\text{CO}$  at  $-14^\circ$  was treated in the course of 2-3 min. with 6.6 cc. of 0.5 *N*  $\text{NaOH}$  at  $0^\circ$  and poured into 80 cc. ice  $\text{H}_2\text{O}$  and the  $\text{As}_2\text{S}_3$ -like ppt. of yellow needles at once filtered on a cold funnel and quickly washed with ice  $\text{H}_2\text{O}$  until neutral to litmus; dried on clay it deflagrates with considerable violence when lightly touched with a Pt spatula and when moistened with alc. evolves the overpoweringly penetrating odor of  $\text{PhN}_2\text{OEt}$ . Again, the clear soln. (10 cc.) resulting from diazotizing 2 g.  $p\text{-MeOC}_6\text{H}_4\text{NH}_2$  in somewhat more than 2 mols.  $\text{HCl}$  with the calcd. amt. of  $\text{NaNO}_2$  gives, when slowly treated at  $0^\circ$  with 20%  $\text{NaOH}$ , a yellow ppt., which explodes when rubbed on clay. From these preliminary expts. B. considers it probable, although not proved, that  $p\text{-ClC}_6\text{H}_4\text{N}(\text{NO})\text{Ac}$  and 1 equiv.  $\text{NaOH}$  gives at first the same diazo anhydride as is obtained by anhydridization of the diazo hydroxide and that the *syn*-diazotates are sec. products of hydrolysis of the nitrosoanilide, produced by the further action of the alkali on the anhydride. This raises again the question as to the chem. nature of the diazo anhydrides. As the result of his earlier works, B. had concluded that they probably have the structure  $(\text{RN})_2\text{O}$  (*Ber.* 29, 450 (1896)) but did not exclude the possibility of a monohexacyclic anhydride structure,  $\text{C}_6\text{H}_4:\text{N}_2$ . The objections then raised against the last structure were never decisive and, under certain assumptions (see below) fall away entirely. Today, B. believes such a structure deserves serious consideration for the following reasons: (1) In a series of diazo hydroxides the  $\text{N}_2\text{OH}$  grouping reacts with an *o*- or *p*-side chain (diazo sulfides, azimides, indazoles, quinone diazides, etc.), but in 1 case (*Ber.* 32, 1773 (1899)) a nucleus H atom of a ring is involved, I passing by "inner condensation" into the yellow II. (2) If the isomerism of the *syn*- and *anti*-diazotates is explained from the stereochem. standpoint it is easy to understand why only the *syn*-hydroxides can form "diazo anhydrides." (3) The action of  $\text{KOH}$  on  $\text{MeN}(\text{NO})\text{CO}_2\text{Me}$  is represented thus:  $\text{MeN}(\text{CO}_2\text{Me})\text{NO} + \text{KOH} \longrightarrow \text{MeN}(\text{CO}_2\text{Me})\text{N}(\text{OK})\text{OH} \longrightarrow \text{KOC}_6\text{H}_5 + \text{MeN}:\text{NOH} \longrightarrow \text{CH}_2:\text{N}_2 + \text{H}_2\text{O}$ ; that on  $\text{PhN}(\text{NO})\text{A}$  thus:  $\text{PhNaAcNO} + \text{NaOH} \longrightarrow \text{PhNaAcN}(\text{ONa})\text{OH} \longrightarrow \text{AcONa} + \text{PhN}_2\text{OH} \longrightarrow$  "diazobenzene anhydride." In connection with the paper on  $\text{Ph}(\text{NO})\text{Ac}$  are reported some expts. of Köpcke. Nitrosodiphenylurea, prepd. from  $\text{CO}(\text{NHPh})_2$  like  $\text{PhN}(\text{NO})\text{Ac}$ , light greenish yellow ppt. of pointed microneedles, m.  $96^\circ$ , cannot be crystd. without decompn.; allowed to stand 3 days in  $\text{C}_6\text{H}_6$ , protected from moisture, it gives  $\text{Ph}_2$ ; with 1 equiv.  $\beta$ -naphthol after some days it yields  $\text{PhN}:\text{NC}_{10}\text{H}_7\text{OH}$ ; with  $\alpha$ -naphthol there at once results a deep red color changing to black but no dye can be isolated. *N*-Nitroso-*p*-bromoacetanilide, m.  $87^\circ$  (deflagration), seps. from gasoline in long light yellowish needles, gives with  $\text{C}_6\text{H}_6$  in  $\text{CHCl}_3$  after some days  $p\text{-BrC}_6\text{H}_4\text{Ph}$ , with  $\beta$ -naphthol in  $\text{CHCl}_3$ ,  $\text{BrC}_6\text{H}_4\text{N}:\text{NC}_{10}\text{H}_7\text{OH}$ , behaves towards  $\alpha$ -naphthol like the preceding compd., yields with  $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$  *p*-bromophenylazo- $\alpha$ -naphthylamine, golden brown felted need-

les from alc., m. 199.5°, sol. in concd.  $H_2SO_4$  with cherry-red color.  $p\text{-ClC}_6H_4N(N\text{:O})Ac$  with  $C_6H_5$  gives  $p\text{-ClC}_6H_4Ph$  and with  $\beta$ -naphthol in  $CHCl_3$   $ClC_6H_4N\text{:NC}_{10}H_7OH$ .



CHAS. A. ROUILLE

Supplementary (remarks) on arylnitramines. EUG. BAMBERGER. *Hidrogenes*. Polytechn., Zürich. *Ber.* 53B, 2321-7(1920).—B. was unable to obtain the Na salt of diazobenzene acid from  $PhNH_2$ ,  $EtNO_2$  and Na in  $Et_2O$ , although he followed Angell's directions carefully; possibly A.'s  $Et_2O$  contained a little  $EtOH$ . When an  $EtOH$ - $Et_2O$  soln. of  $KOEt$  was substituted for Na the expt. was successful; to 1.5 g. K, 4.3 g.  $EtOH$  and 4.3 g.  $Et_2O$  was added 3.45 g.  $EtNO_2$  and, after 70-80 sec., 3.5 g.  $PhNH_2$  and a little  $Et_2O$ ; after 2 hrs. the resulting cryst. magma was filtered, washed with 10-5 cc.  $Et_2O$  and the crystals of K salt (2.86 g.) treated in concd. aq. soln., with vigorous stirring, with a little more than the calcd. amt. of  $BaCl_2$ , the Ba salt filtered at 0°, sparingly washed with ice  $H_2O$  till free from Cl (it now weighed 2.6 g.), converted with the usual precautions into  $PhNHNH_2$ , at once exhaustively extd., without filtering, with  $Et_2O$ , freed from any HCl with ice  $H_2O$ , repeatedly extd. with concd.  $NH_4OH$ , concd. and acidified, the  $PhNHNH_2$  sepg. in silvery needles melting somewhat low (43-4°). The yield was 1.55 g. (47%); Angell obtained considerably less (but with the right m. p.) while B.'s old method (from the isodiazotate and  $K_3Fe(CN)_6$ ; *Ber.* 27, 915(1894)) gives more than 80%. As the m. p. of the compd. prepd. in the above manner is a few degrees too low, it may possibly (?) be contaminated with another explosive acid (or pseudo acid) which was formed when the  $EtNO_2$  and  $PhNH_2$  were added together, not separately, to the  $KOEt$  soln.; thus, when 4.92 g. K in  $EtOH$ - $Et_2O$  was slowly treated with a mixt. of 11.5 g.  $EtNO_2$  and 11.75 g.  $PhNH_2$ , the liquid became turbid in about 15 min. and overnight deposited faintly straw-yellow microleaves; these were acidified in cold  $H_2O$  under  $Et_2O$ ; then washed, dried (with  $Na_2SO_4$ ) and cautiously concd.  $Et_2O$  ext. deposited in a vacuum desiccator yellow crystals, a minute amt. of which, heated in a capillary for a m. p. detn., exploded at 70-6° with a loud report and such violence that a round hole was blown through the middle of the thick-walled beaker used as the bath. The reduction of the  $PhNHNH_2$  to isodiazobenzene is effected (better than with  $Na$ - $Hg$ ) with a little Zn dust and  $NH_4Cl$  in very dil. aq. soln.; under these conditions no  $PhNHNH_2$  is formed. To the earlier description of *O*-diazobenzene acid Me ether (*Ber.* 30, 1250(1897)) must be added that it decomp. on dry distn. into  $HCHO$ ; other *O*-ethers of diazo acids still available were found to react in the same way. The reaction is so sensitive that very small amts. of the ethers can be detected by the aldehyde odor. The decompn. is probably similar to that of the analogously constituted *C*-nitronic acid ethers (e. g.,  $MeC(N:NPh):N(O)OMe$ ; *Ber.* 36, 91(1903)), and of the amine oxides having the grouping  $=N(O)Me_2$  (C. A. 3, 172); in all these cases it seems to be the complex  $=N(O)OMe$  or  $=N(O)Me$  which decomp. into  $HCHO$  and  $=NOH$  or  $=NH$ . 1-Nitro-3,5-dimethylphenyl-6-nitramine (A), having 2 substituents in the  $\alpha$ - and 1 in the  $\beta$ -position (v. Goldberger, *Diss. Zürich*, 1897 115), does not undergo the rearrangement into a nucleus-nitrated aniline which otherwise is so easily effected in aryl-nitramines; instead, the chief reaction is a reduction to the corresponding diazonium salt ("auto-diazotization," *Ber.* 30, 1249(1896)); a considerable part of the A remains unchanged, another part resinifies. 1-Nitro-3,5-xylidine 6-isodiazotate,  $Me_2(O_2N)C_6H_3N_4OK$  (5.3 g. from 5 g.  $Me_2(O_2N)C_6H_3NH_2$  rubbed with 9.4 cc. concd. HCl, diazotized with 2.2 g.  $NaNO_2$  in a very little  $H_2O$ , dild. with 50 cc. ice  $H_2O$ , poured into 60 g. KOH

in 60 g.  $H_2O$  below  $10^\circ$ , treated with 10–20 g. stick KOH, warmed to about  $50^\circ$  until a clear soln. is obtained, cooled, pressed out and dried on clay, light yellow leaflets, stable for weeks in a KOH desiccator in the dark; 10 g. added to 15 g.  $K_3Fe(CN)_6$  and 1.5 g. KOH in 90 g. cold  $H_2O$ , allowed to stand in the ice chest 48 hrs., then 2 days at room temp., and a few hrs. on a  $H_2O$  bath, cooled, filtered, shaken several times with  $Et_2O$ , acidified at  $0^\circ$  with dil.  $H_2SO_4$ , extd. with  $Et_2O$ , extd. from the  $Et_2O$  with aq.  $NH_4OH$ , concd., boiled with charcoal, partially neutralized with AcOH and pptd. with  $H_2SO_4$ , gives 3 g. A, long straw-yellow needles from ligroin, sinters  $89^\circ$ , m.  $90-1^\circ$ , deflagrates on the Pt foil with relatively little noise. The  $Et_2O$  ext. of the alk. oxidation mixt. contains some 3,5-Me $_2C_6H_3NO_2$ , m.  $70.5-1.0^\circ$ . A (1 g.) in 3 cc. AcOH treated at  $0^\circ$  with a mixt. of 1 cc. each of  $H_2SO_4$  and AcOH at once gives a yellow magma and the odor of  $HNO_3$ ; after 4 hrs. in the ice chest the soln. (which in the meantime has become clear and dark) is poured into ice  $H_2O$ , which ppts. 0.3 g. of unchanged A mixed with tar; the filtrate is at once exhaustively extd. in the cold with  $Et_2O$  and then poured into an alk. soln. of 0.7 g.  $\beta$ -naphthol; this gives 0.45 g. of the dye, 3,5,6-Me $_3(HOC_{10}H_6N_2)_2C_6H_3NO_2$ , red needles with green reflex from alc. or xylene, m.  $104.5^\circ$ , identical with that obtained from diazotized 3,4,6-Me $_3(H_2N)C_6H_2NO_2$  and  $\beta$ -naphthol. The  $Et_2O$  ext. contains, besides a little A, traces of a primary base (sepd. by shaking the  $Et_2O$  soln. with NaOH) which m. (impure)  $66^\circ$  and is probably 3,5,6-Me $_3(H_2N)C_6H_2NO_2$ . C. A. R.

**Methylations with diazomethane in the uric acid series.** HEINRICH BILTZ and FRITZ MAX. Univ. Breslau. *Ber.* 53B, 2327–42 (1920).— $CH_3N_2$  does not react at all with uric acids alkylated in positions 3 and 9 but does react with all those acids which are not substituted in position 9, giving 1,3,7-trimethyl-8-methoxyxanthine (A) while those alkylated at 9 but not at 3 give 1,7,9-trimethyl-2-methoxy-6,8-diketopurine (B), isomeric with A. B. and M. believe that the H atom (at 9 or 3) by first enolizing makes possible the formation of a MeO compd. which, possibly on account of increased soly., is then further methylated on the N, position 9 being first occupied if it is not already alkylated, then 3, while 1 and 7 stand far behind in their reactivity. The behavior of the salts of the uric acids leads to the same conclusions, as do the results so far obtained in an investigation now in progress on the direct measurement of the acidity of the individual H atoms in the acids. One expt. with  $MeCHN_2$  led to the same result as those with  $CH_3N_2$ . Entirely different is the action of  $CH_3N_2$  on uric acid glycols, their di- and their hemiethers. The hemiethers take up only 1 new Me group in position 9; if this is occupied there is no reaction. The diethers also take up only 1 Me group but in position 1. The glycols, insofar as they react, are methylated on the HO at 5 and also on the N at 9 if this position is not occupied. It is as yet impossible to formulate the laws which govern the entrance of Me into the glycols and their ethers; apparently, however, the reactivity of the 3- and 9-H atoms in the acids is very materially dependent on the 4,5-double bond which is absent in the glycol ethers. A 4-HO group seems to have a similar but less pronounced influence on a 9-H atom. The reactivity of the 1-H atom in the diethers seems to be related with the *p*-MeO group at 4. In carrying out the expts. 10–5 cc. of an  $Et_2O$  soln. of  $CH_3N_2$  was added to 0.3–0.5 g. of the very finely powdered dry substance, the reactivity of which was judged by the rate of evolution of N. The flasks were allowed to stand, loosely stoppered, overnight, most of the  $Et_2O$  was evapd. off at room temp., the residue broken up and powdered, again treated with  $CH_3N_2$  and, when the yellow color persisted overnight, evapd. at room temp. and worked up. A was formed quant. by 1,3,7-tri- and 1,3-, 1,7- and 3,7-dimethyluric acids. 1- and 7-Methyluric acids required several treatments with  $CH_3N_2$ , and the 3-Me isomer reacted with special sluggishness; uric acid itself reacted vigorously but naturally required much  $CH_3N_2$ , and it was essential to rub the product carefully before each fresh addition of  $CH_3N_2$ ; all these acids yielded A. B. crystals from alc., m.  $188-97^\circ$ , smoothly

rearranges into 1,3,7,9-tetramethyluric acid (C) after 15 min. at 205°, was obtained from 1,7,9-tri-, 7,9- and 1,9-di- and 9-monomethyluric acids, the reactivity decreasing in the order given; 0.5 g. of the 1,7,9-acid gave, besides 0.4 g. B, about 0.1 g. C. 3,7,9- and 1,3,9-Tri- and 3,9-dimethyluric acids did not react. From 0.5 g. 1,3-dimethyl-7-ethyluric acid (B. and Zellner, in a forthcoming number of the *Ann.*) were obtained 0.8 g. 1,3-dimethyl-7-ethyl-8-methoxyxanthine, prisms from alc., m. 135°, rearranges into 1,3,9-trimethyl-7-ethyluric acid (D) when moistened with a drop of MeOH and heated 1-2 hrs. at about 200°, and 0.2 g. D, crystals from alc., m. 215°. 1,7,9-Trimethyl-2-ethoxy-6,8-diketopurine (0.3 g. from 0.4 g. 1,7,9-trimethyluric acid and  $\text{McCHN}_3$ ), fine needles m. 149°, rearranges after 2 hrs. at 230° in a sealed tube into 1,7,9-trimethyl-3-ethyluric acid, tablets from alc., m. 240-1°. 1,3-Dimethyluric acid glycol Me and Et hemiethers give the corresponding 1,3,9-trimethyl ethers, m. 194° and 138°; 3,7-dimethyluric acid glycol Me hemiether yields the 3,7,9-tri-Me ether, m. 186-7°; from 7-methyluric acid glycol Et hemiether is obtained the 7,9-dimethyl ether, m. 185°; 7-ethyluric acid glycol Et hemiether forms the 7-ethyl-9-methyl ether, m. 193°. The above methylated ethers will be described in a series of papers to appear in the *Ann.* 3,9- and 7,9-di- and 3,7,9-Trimethyluric acid glycol Me hemiethers do not react with  $\text{CH}_2\text{N}_2$ . Uric acid glycol di-Me ether smoothly gave 1-methyluric acid glycol di-Me ether, m. 225° (decompn.). 3,7-, 7,9- and 3,9-Dimethyluric acid glycol di-Me ethers yielded the 1,3,7- (m. 178-9°), 1,7,9- (m. 152°) and 1,3,9- (tables from  $\text{H}_2\text{O}$ , sinters 120°, m. 128°) trimethyl ethers. 1-Mono-, 1,4-di- and 1,3,7-trimethyluric acid glycol di-Me ethers did not react with  $\text{CH}_2\text{N}_2$ . 7,9-Dimethyluric acid glycol smoothly gave the methyl hemiether, m. 185°; 3,7-dimethyluric acid glycol yielded 3,7,9-trimethyluric acid glycol Me hemiether, m. 185°; uric acid glycol hemihydrate and its anhydride and 9-mono- and 3,9-dimethyluric acid glycols did not react. 1,7-Dimethyl-*spiro*-5,5'-dihydantoin yielded the tetra-Me compds., m. 228-9°.

C. A. ROULLIER

**Tri-*o*-anisylltelluronium salts.** KARL LEDERER. *Prag. Ber.* 53B, 2342-6 (1920); cf. C. A. 11, 2670; 14, 3234.—The reaction between  $\text{TeCl}_4$  and *o*- $\text{MeOC}_6\text{H}_4\text{MgBr}$  does not proceed entirely according to the equation  $\text{TeCl}_4 + 3\text{RMgBr} = \text{R}_3\text{TeCl} + 3\text{MgClBr}$ ; a part of the  $\text{TeCl}_4$  is reduced to Te and some of the  $\text{R}_3\text{TeCl}$  to  $\text{R}_2\text{Te}$ , thus:  $\text{TeCl}_4 + 4\text{RMgBr} = \text{Te} + 4\text{MgClBr} + 2\text{R}_2\text{Te}$  and  $\text{R}_3\text{TeCl} + \text{RMgBr} = \text{R}_2\text{Te} + \text{R}_3 + \text{MgClBr}$ . Ten g.  $\text{TeCl}_4$  in about 250 cc. cold  $\text{Et}_2\text{O}$  is quickly mixed with 35.8 g. *o*- $\text{MeOC}_6\text{H}_4\text{Br}$  and 4 g. Mg in 100 cc.  $\text{Et}_2\text{O}$ , quickly stirred, treated cold with 15-20 cc.  $\text{H}_2\text{O}$ , filtered, dried *in vacuo*, extd. twice with  $\text{CHCl}_3$ , concd. to 50 cc., dropped into 0.5 l. boiling  $\text{H}_2\text{O}$ , filtered from a small amt. of brown tar, treated with a little  $\text{SO}_2$  and then, boiling hot, with 10 g. KI in a little  $\text{H}_2\text{O}$ ; on cooling, tri-*o*-anisylltelluronium iodide seps. in long, silky, asbestos-like fibers (yield, 5.2-8.6 g.; the  $\text{Et}_2\text{O}$  filtrate yields 4-6 g. dibromide). The iodide seps. from xylene in flocks (the soln. is faintly violet, indicating decompn.); after 2 crystals. from  $\text{Et}_2\text{O}$ - $\text{EtOH}$ , it softens 187-8°, m. turbid 190°, clear 191-2°; from  $\text{H}_2\text{O}$  it seps. in crystals with 2  $\text{H}_2\text{O}$ , softens 124°, m. 126-7°; iodide-mercuric iodide salt,  $\text{C}_6\text{H}_3\text{O}_2\text{TeI.HgI}_2$ , from the components in alc., faintly yellowish ppt., sinters 229°, m. 234-5°; chloride, from the iodide in  $\text{H}_2\text{O}$  boiled with excess of  $\text{AgCl}$ , fine felted silky needles with 4  $\text{H}_2\text{O}$ , m. about 112°, foams 116°, seps. from  $\text{EtOH}$ - $\text{Et}_2\text{O}$  in fine felted needles with 1  $\text{EtOH}$ , m. 114°, foams 118° on rapid heating, sinter 170-1°, m. 175-6° on slow heating; mercuric chloride salt, from the components in  $\text{H}_2\text{O}$ , white ppt., begins to decomp. 234°, m. 236-7°, columns from alc., soften 240°, m. 244-5°; picrate, from the components in  $\text{H}_2\text{O}$ , 6-sided prismatic columns (mixed with solidified oily droplets) from alc., softens 160°, m. 169-70°; bromide, from the chloride and KBr in  $\text{H}_2\text{O}$ , hair-like silky felted needles with 2  $\text{H}_2\text{O}$ , softens 109°, m. 112° in its  $\text{H}_2\text{O}$  of crystn., solidifies and m. again 194-5° (slight decompn.), seps. from  $\text{EtOH}$ - $\text{Et}_2\text{O}$  in fine needles with 1  $\text{EtOH}$ , softens above 100°, solidifies and m. again 202-3°; when solvent-free, it begins to soften 106° and m.

202–3° (foaming); mercuric bromide salt, loose powder from H<sub>2</sub>O, begins to sinter 186° m. about 218°.

C. A. R.

**Dimethylaminobenzenesulfonic esters and the nucleus-nitrosation of *N*-methyl-anilinesulfonic acid.** J. HOUBEN AND G. SCHREIBER. Univ. Berlin. Ber. 53B, 2346–51 (1920).—*o*-MeNHC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H (A) (10.8 g. from 15 g. *o*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H in 35 cc. H<sub>2</sub>O and 4.7 g. soda shaken with 11 g. Me<sub>2</sub>SO<sub>4</sub>), crystals from MeOH, decomp. 220°, also obtained in 12-g. yield, quite pure, from 30 g. of the com. H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na in 60 cc. cold H<sub>2</sub>O with 19.5 g. Me<sub>2</sub>SO<sub>4</sub>. Methyl-*o*-dimethylaminobenzenesulfonate is prepd. from 20 g. H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H (obtained from the com. Na salt with dil. H<sub>2</sub>SO<sub>4</sub> (8.9 g. acid from 15 g. salt)) and crystd. from glacial or dil. AcOH or from MeOH heated under a reflux with 75 cc. Me<sub>2</sub>SO<sub>4</sub> until dissolved, cooled, and treated with Et<sub>2</sub>O, which takes out unchanged Me<sub>2</sub>SO<sub>4</sub> and leaves a thick sirup; the Et<sub>2</sub>O layer is extd. with dil. H<sub>2</sub>SO<sub>4</sub> with which the sirup is dissolved and the ester is pptd. by cautious neutralization in the cold with soda, extd. with Et<sub>2</sub>O, dried with Na<sub>2</sub>SO<sub>4</sub>, evapd., freed from the last traces of Et<sub>2</sub>O *in vacuo* and at once crystd. from petr. ether or C<sub>6</sub>H<sub>6</sub>-petr. ether, from which it seps. in needles. Methyl *N*-dimethylsulfanilate (6.5–7.0 g. from 25 g. *p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H heated with 42 cc. Me<sub>2</sub>SO<sub>4</sub> under a reflux at 170–80° until completely dissolved), leaflets from alc. or from ligroin, needles from H<sub>2</sub>O or Et<sub>2</sub>O. Methyl *N*-dimethylmetanilate is prepd. like the *p*-compd. and crystd. from alc. A (4 g.) in 50 cc. each of cold H<sub>2</sub>O and dil. HCl treated with 1.5 g. NaNO<sub>2</sub> in a little H<sub>2</sub>O, allowed to stand 1 day in the ice chest, evapd. *in vacuo* over H<sub>2</sub>SO<sub>4</sub>, treated with a little fuming HCl, and again evapd. *in vacuo*, yields a yellow-brown substance, probably the crude hydrochloride (B) of 4,2-ON-(MeNH)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>H resulting by rearrangement in the concd. HCl of *o*-HO<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>N(NO)-Me first formed; the salt gives with aq. soda a green soln. showing all the typical color reactions of NO compds. If 8 g. of the crude A is shaken with 65 cc. fuming HCl and slowly treated in the cold with 4 g. finely powdered NaNO<sub>2</sub>, the resulting red-brown liquid deposits on frequent shaking in a freezing mixt. the crude yellow B which after standing 3 days in the ice chest is filtered and dried *in vacuo* over powdered NaOH (yield, 8.4 g.); when dry it is stable. On rubbing with NaOAc or soda soln. it loses its HCl but the free 2-methylamino-5-nitroso-benzenesulfonic acid could not be isolated; it is unusually sol. in H<sub>2</sub>O, insol. in Et<sub>2</sub>O; ammonium salt (2 g. from 3 g. crude B shaken in a little dil. NH<sub>4</sub>OH at 0°), dark blue to steel-blue crystals from MeOH forming a dark green powder, decomp. without melting, burns explosively on Pt foil, changed to brown by concd. NaOH but not by concd. NH<sub>4</sub>OH or soda; potassium salt, from B in a little satd. K<sub>2</sub>CO<sub>3</sub> with concd. KCl, green leaflets; sodium salt, from the NH<sub>4</sub> salt in H<sub>2</sub>O with concd. NaCl at 0°, green needles; barium salt, light green needles; AgNO<sub>3</sub> gives a brown ppt. sol. on heating with green color. The NH<sub>4</sub> salt condenses in dil. alc. soln. with *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CN and NaOMe to an orange azomethine; the NH<sub>4</sub> salt or B gives with gallic acid in the presence of AcOH and concd. HCl a reddish violet, with  $\alpha$ -C<sub>10</sub>H<sub>7</sub>NH $\beta$ t a red dye, with  $\beta$ -naphthol a red color; the NH<sub>4</sub> salt with PhNHNH<sub>2</sub>·HCl forms a yellow substance. When 4 g. of the crude NH<sub>4</sub> salt is dissolved in 20 cc. of 30% NaOH and 120 cc. of H<sub>2</sub>O an intense odor of MeNH<sub>2</sub> and NH<sub>3</sub> is at once evolved and the red-yellow soln. gradually becomes deep dark red; after 2 hrs. much alc. ppts. in the cold a brown-green flocculent ppt. easily sol. in AcOH and repptd. by Et<sub>2</sub>O. A Na detn. of the crude product extd. with abs. alc. indicates that the product is not homogeneous. The alc. ext. deposits on standing a light green product easily sol. in H<sub>2</sub>O with red-brown color and repptd. by alc., insol. in Et<sub>2</sub>O and sol. almost without color in dil. H<sub>2</sub>SO<sub>4</sub>; it is probably sodium-2-hydroxy-5-nitrosobenzenesulfonate.

C. A. ROULLER

**Nitrososalicylic acid and nitrosoanthranilic acid.** J. HOUBEN AND G. SCHREIBER. Univ. Berlin. Ber. 53B, 2352–62 (1920).—5-Nitroso-*N*-methylanthranilic acid sulfate, HO<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>(NOH)(NMe).H<sub>2</sub>SO<sub>4</sub>, a yellow substance stable in the air, is obtained,

together with  $\text{HOCC}_6\text{H}_4\text{NHMe.H}_2\text{SO}_4$  from 5 g. *o*-MeNHC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H (A) in concd. HCl treated with 4.2 g. dry O<sub>2</sub>NSO<sub>3</sub>H, also from 5 g. A in 40 cc. of a cold mixt. of 30 g. concd. H<sub>2</sub>SO<sub>4</sub> and 70 g. AcOH (or 20:80) slowly treated with 2.5 g. finely powdered NaNO<sub>2</sub>. It has been found that nucleus-nitrosation is best effected in concd. HCl with NaNO<sub>2</sub> protected from the air; 5,2-ON(MeNH)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>Me (B) was accordingly prepd. from 25 g. of the Me ester of A in 188 cc. cold concd. HCl in a 500-cc. stoppered flask slowly treated with continuous shaking with 15 g. finely powdered NaNO<sub>2</sub>, filtered after 40-8 hrs., washed with very little concd. HCl and decompd. with about 1 l. H<sub>2</sub>O, yielding 10.7 g. B; the filtrate with soda or dil. NH<sub>4</sub>OH gives a further 15 g. The portion obtained by decompn. of the HCl salt is pure and light green; that obtained by pptn. is purified by crystn. from much H<sub>2</sub>O, or, better, from ligroin. The Et ester of A can be prepd. not only by the Hans Meyer method but also (in 78% yield) by the usual way if the esterification with EtOH and H<sub>2</sub>SO<sub>4</sub> is interrupted only after the formation of Et<sub>2</sub>O has begun (for details, cf. Schreiber, *Diss. Berlin* 1915, 30). It b<sub>10</sub> 141-3° and solidifies in well defined crystals. The nitrosation is effected as described above for the Me ester but none of the product seps. as the HCl salt; the whole of the NO ester is pptd. from the soln. (strongly cooled and highly dild. with H<sub>2</sub>O) with dil. NH<sub>4</sub>OH or soda as a light green substance, m. 89° after crystn. from ligroin, petr. ether, alc. or H<sub>2</sub>O; 31 g. of the ester of A thus nitrosated in 248 cc. HCl yields 32.2 g. crude NO ester. The free NO acid is similarly obtained by allowing the finely powdered NaNO<sub>2</sub> to act 48 hrs. in ice on a concd. HCl soln. of A in the presence of glass beads and shaken in a machine; yield, over 80%. While concd. alkalis not only split off NH<sub>4</sub>Me from B but also sapon. the ester grouping, *methyl 5-nitrososalicylate* (C) can be obtained by steam distn. of a soln. of B in dil. H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>; even under these conditions, however, the yield is small, as after a short time side reactions set a limit to its formation; all efforts to obtain better yields by modifying the conditions failed (distn. in aq. NaHSO<sub>4</sub>, dropping the soln. in dil. H<sub>2</sub>SO<sub>4</sub> into highly dild. H<sub>2</sub>SO<sub>4</sub> through which steam was being passed); it was found best to distil small portions in dil. H<sub>2</sub>SO<sub>4</sub>. Thus 2 g. B in 50-60 cc. dild. H<sub>2</sub>SO<sub>4</sub> with steam gives 0.3-0.6 g. crude C sepg. in the cooled receiver in blue flocks (extrn. of the filtrate with Et<sub>2</sub>O gives only a very small amt. of a mixt. of unchanged B and of C); the crude C is best freed from the small amt. of accompanying B by making alk. with soda, extg. the undissolved C with Et<sub>2</sub>O and pptg. with dil. H<sub>2</sub>SO<sub>4</sub>, all the operations being carried out as rapidly as possible to prevent sapon. in the alk. soln. The C seps. from petr. ether in blue cubes or octahedrons, m. 89-90°, sol. in alkali alcohols free from H<sub>2</sub>O with green color changing to red-brown on addition of H<sub>2</sub>O; dry NH<sub>3</sub> ppts. from the blue-green soln. of C in Et<sub>2</sub>O the green *ammonium salt*, sol. in a little H<sub>2</sub>O with red-brown color. In aq. alkalis C and the Et ester yield at once red-brown solns. from which, if not too dild., the Et ester usually seps. spontaneously, C on salting out with NH<sub>4</sub> salts, as the green alkali salt which redissolves on shaking with much H<sub>2</sub>O. Dil. H<sub>2</sub>SO<sub>4</sub> reppts. the light blue esters from the red-brown alk. solns. With PhCH<sub>2</sub>CN the esters condense in alc., containing a few drops of NaOMe, on heating to yellow, with *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CN to orange azomethines. The Et<sub>2</sub>O soln. of C is turned yellow by a few drops of PhNHNH<sub>2</sub> and deposits with violent evolution of N<sub>2</sub> a yellow substance quite sol. in Et<sub>2</sub>O, probably *methyl azoxysalicylate*, [4,3-HO(MeOC)C<sub>6</sub>H<sub>3</sub>-N<sub>2</sub>O], sol. in concd. H<sub>2</sub>SO<sub>4</sub> with red color which persists on adding ice after heating. If the C is rubbed with PhNHNH<sub>2</sub>.HCl and a few drops of H<sub>2</sub>O a yellow product is formed but no N is evolved. *Ethyl 5-nitrososalicylate* (D), blue needles from petr. ether, m. 47-8°, condenses with  $\beta$ -naphthol in AcOH and concd. HCl to a violet and with gallic acid to a malachite-green dye; PhNH<sub>2</sub>.HCl gives a red-brown soln. *Methyl 5-nitroso-anthranilate*, from 1 g. C heated on the H<sub>2</sub>O bath 30-40 min. until the green mass just becomes brown, with 5 parts NH<sub>4</sub>Cl, 10 parts dry NH<sub>4</sub>OAc and a little (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>,

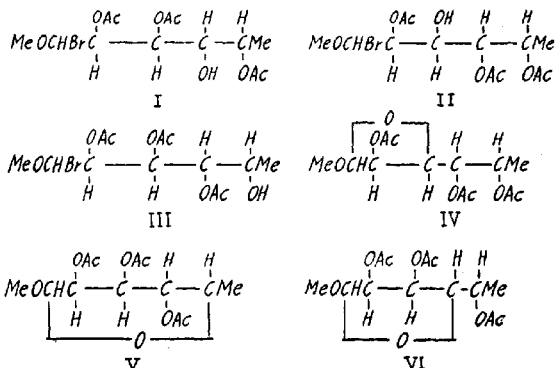
cooled, extd. with  $H_2O$ , shaken with  $Et_2O$ , extd. from the  $Et_2O$  with dil.  $HCl$  and pptd. in the cold with soda (yield, 0.3 g.; the  $Et_2O$  soln. on evapn. yields 0.6 g. unchanged C), long dark green dichroic needles from  $H_2O$ , sublimes in light green needles, m. 167–8°. *Ethyl ester* (0.55 g. from 1 g. D), dichroic (green and violet-blue) needles from  $H_2O$ , m. 139°, condenses with  $p-O_2NC_6H_4CH_2CN$  in the presence of a little  $NaOMe$  to a yellow to orange azomethine, gives with  $\alpha$ -naphthol in  $AcOH$  and concd.  $HCl$  a red-violet, with  $PhNH_2.HCl$  a red-brown soln., with gallic acid a deep violet dye. *Free acid hydrochloride* (1.25 g. from 2 g. 2,5-HO(ON) $C_6H_4CO_2H$ , 10 g.  $NH_4Cl$ , 20 g.  $NH_4OAc$  and a little  $(NH_4)_2CO_3$  heated 5–7 min. at 130–40°, cooled, dissolved as completely as possible in the calcd. amt. of dil.  $HCl$  (54 cc.) and  $H_2O$  and extd. with  $Et_2O$  which is then shaken with 15–20 cc. dil.  $HCl$ ), seps. in light yellow needles with 1  $H_2O$ , easily sol. in alc. with brown color, decomp. on heating without melting, condenses in alc. with  $PhCH_2CN$  and  $p-O_2NC_6H_4CH_2CN$  and a few drops  $NaOMe$  to yellow and orange azomethines, resp., forms with gallic acid and  $\alpha$ -naphthol in  $AcOH$  and concd.  $HCl$  violet dyes, gives with  $PhNH_2.HCl$  a brown to violet ppt.; when it is decompd. by rubbing with  $H_2O$  the free acid (E) seps. only in the first instant as a pure green substance which soon becomes dark green and discolored, probably as a result of the oxidation of the  $NH_2$  group. It may also be obtained in impure form directly from the melt when the  $HCl$  soln. of the  $HCl$  salt sepd. from the  $Et_2O$  is cautiously treated with  $NH_4OH$  in the cold until it is still just acid, also by heating the ester several hrs. under a reflux with dil.  $NH_4OH$  and pptg. by cautious neutralization with dil.  $HCl$ . The light green *sodium* and *ammonium salts* are obtained by rubbing the  $HCl$  salt with satd.  $NaOAc$  and  $NH_4OH$ , resp. The Na salt dissolves in concd. alkalies with red-brown color. The  $NH_4$  salt dissolves in the slightest excess of  $NH_4OH$  with brown color and in abs.  $MeOH$  through which dry  $NH_3$  is passed;  $Et_2O$  repts. it in green flocks.

CHAS. A. ROUILLER

Acetobromorhamnose and its use for the synthesis of rhamnosides. EML. FISCHER, MAX BERGMANN AND ARTUR RABE. Univ. Berlin. *Ber.* 53B, 2362–68 (1920).—Of the two general methods for the synthesis of alc. glucosides—treatment of the sugar with the alc. and  $HCl$  and of acetobromoglucose with the alc. in the presence of a reagent to combine with the  $HBr$  and subsequent deacetylation—the second has in difficult cases almost always proved the more satisfactory, as apparently only one glucoside (the  $\beta$ -form) is formed in this process; the first stage in the reaction, therefore, seems to consist essentially of a replacement of the halogen by the alc. residue. Entirely different results were obtained, however, when the method was applied to *acetobromorhamnose* (A). When this is treated with  $MeOH$  and  $Ag_2CO_3$ , there are formed 3 isomeric methylrhamnoside triacetates, all differing from the triacetate prepd. from the only known rhamnoside (B). There are thus 4 methylrhamnoside triacetates,  $C_{12}H_{20}O_8$ , all of which reduce Fehling soln. only after hydrolysis with dil. acids and hence have the  $MeO$  group on the so-called aldehyde C atom. Thinking that the multiplicity of the products obtained with A might be due to the A itself being a mixt. of isomers many painstaking efforts were made to sep. it into components of differing properties, but without success. That it has the furan structure, like acetobromoglucose, and not, possibly, another, more labile cyclic structure, is shown by expts., to be reported in detail later, by which A can be converted without difficulty into a substance of pronounced furan properties, the so-called rhamnal. As a considerable portion of the methylrhamnoside acetates obtained from A (the  $\gamma$ - and apparently also the  $\delta$ -form described below) have not a furoid constitution, there must occur, in their formation, an expansion or a contraction of the O ring with a simultaneous migration of an Ac group. Possibly the key to the complicated process is to be sought in the assumption that the glucoside formation is initiated by the addition of the alc. to the A in such a way that there is



first an opening of the furan ring, yielding a compd. of the type I, a deriv. of the oxoform of rhamnose having the characteristics of a partially acylated polyhydric alc., compds. which often show a pronounced tendency to rearrange intramol., with a shifting of the acyl groups (C. A. 15, 687). I, by a migration of the Ac at 3 or at 5 to the free HO group at 4, would give the compds. II and III which might undergo still further rearrangement. Under the influence of the HBr-binding substance ( $\text{Ag}_2\text{CO}_3$  in the present case), the ring would be closed again, with formation of the compds. IV and V. II, however, the  $\text{Ag}_2\text{CO}_3$  reacts with I before it rearranges, there will be formed a compd. VI of the hydrofuran type. It may well be conceived that in many cases, such as with acetobromoglucose, one of the competing reactions is so favored at the expense of the others that the resulting product is apparently homogeneous. It will probably soon be found that the formation of isomeric glucoside acetates in this reaction is not limited to the rhamnosides, also that varying the alc. constituent may produce changes in the results and finally, in cases where isomers are formed, that their relative amts. will vary with the nature of the HBr-binding substance used. The authors have already found



that with A when quinoline is used instead of  $\text{Ag}_2\text{CO}_3$  none of the  $\beta$ -acetate is formed while much of the  $\gamma$ - and considerable of the  $\delta$ -forms are produced, also that A with menthol yields several isomers. When 100 g. crystd. rhamnose in 400 cc.  $\text{C}_2\text{H}_5\text{N}$  at  $0^\circ$  is slowly treated with 400 cc.  $\text{Ac}_2\text{O}$ , allowed to stand 20 hrs. at room temp., and poured into ice  $\text{H}_2\text{O}$  and the resulting viscous oil is taken up in  $\text{Et}_2\text{O}$ , washed with  $\text{H}_2\text{SO}_4$ ,  $\text{KHCO}_3$  and  $\text{H}_2\text{O}$  and dried with  $\text{CaCl}_2$  there is obtained 135 g. of a light yellow sirup consisting chiefly of rhamnose tetraacetates (C 50.42, H 6.19% after 2 distns. under 0.3 mm. at a bath temp. of  $160^\circ$ ) from which there occasionally seps. a small amt. of a cryst. product, provisionally designated as the  $\alpha$ -tetraacetate (C), prisms from 50% alc., m.  $98-99^\circ$ ,  $[\alpha]_D^{20}$  14.08° in  $(\text{CHCl}_3)_2$ . The crude product (100 g.) in 50 cc.  $\text{AcOH}$  at  $0^\circ$  treated with 200 g. of  $\text{AcOH}$  satd. with HBr, allowed to stand 1.5 hrs. at room temp., dild. with 400 cc.  $\text{CHCl}_3$ , carefully washed 2-3 times with ice  $\text{H}_2\text{O}$ , at once dried a short time with  $\text{CaCl}_2$  and evapd. *in vacuo* (finally at  $50^\circ$ ) gives a somewhat yellow sirup which, treated in a little  $\text{Et}_2\text{O}$  with 2-3 parts petr. ether, persistently rubbed and allowed to stand a long time in the ice chest, yields a thick cryst. magma which, after draining and superficial drying in the air, is taken up in 120 cc.  $\text{AmOH}$  and treated with 240 cc. petr. ether; on rubbing and cooling A (70 g.) seps. in needles, m.  $71-2^\circ$ ,  $[\alpha]_D^{20}$  -168.97° in  $(\text{CHCl}_3)_2$ , quite sensitive towards  $\text{H}_2\text{O}$ , soon decomp. completely in moist air but is

stable, for months over  $P_2O_5$  and soda-lime, easily exchanges its Br for HO when treated with  $Ag_2CO_3$  and  $H_2O$ , and gives, depending on the conditions, two different cryst. triacetylramnosides:  $\alpha$ -form, from 10 g. A in 100 cc. moist  $Me_2CO$  at  $0^\circ$  shaken 30 min. with 8 g. dry  $Ag_2CO_3$ , filtered, evapd. *in vacuo* below  $25-30^\circ$ , dissolved as quickly as possible, with warming and shaking, in 20 cc. dry  $Et_2O$  and allowed to stand 1 hr. in a freezing mixt. (yield, 6 g.), 4- to 6-sided plates, m.  $96-8^\circ$ , shows mutarotation in alc.,  $CHCl_3$  and  $(CHCl_3)_2$ ,  $[\alpha]_D^{21}$   $28.11^\circ$  in alc. 10 min. after soln., the rotation gradually decreasing and finally becoming negative ( $-18.6^\circ$  after 8 days at  $15-20^\circ$ ); heating and addition of  $H_2O$  and especially of  $C_6H_5N$  greatly accelerate the change; if a soln. is allowed to stand until the rotation no longer changes and is then concd. the  $\beta$ -triacetate seps. in rodlets, sinters around  $100^\circ$ , m.  $115^\circ$  (decompn.),  $[\alpha]_D^{18}$   $-19.4^\circ$  (alc.), shows no mutarotation; this last fact, in connection with the indefinite m. p., makes it probable that the product is really a mixt. of the  $\alpha$ -form with an unknown highly *l*-rotatory isomer; exhaustive acetylation yields a sirupy tetraacetate whereas 2 g. of the  $\alpha$ -form allowed to stand 20 hrs. at  $0^\circ$  in 1.5 cc. each of  $C_6H_5N$  and  $Ac_2O$ , poured into 20 cc. ice  $H_2O$  and allowed to stand 2 hrs. at  $0^\circ$  gives 1.85 g. C. When 25 g. A in 250 cc. dry MeOH is shaken with 25 g. dry  $Ag_2CO_3$ , evolution of  $CO_2$  begins at once and in 40 min. the soln. is free from Br; it is filtered, evapd. *in vacuo* at  $35^\circ$ , taken up in 40 cc. hot alc. and allowed to stand several hrs. in a freezing mixt., 20 cc.  $H_2O$  being slowly added; the crude cryst. product (11-2 g.) is boiled in 40 cc. alc. with charcoal, dild. with 120 cc.  $H_2O$  and cooled to  $0^\circ$ , giving 7-8 g. of a pure white product consisting of a mixt. of  $\beta$ - and  $\gamma$ -methylramnoside triacetates, needles and cubes, resp., which are sepd. by a combined mechanical sepn. and fractional crystn. from ligroin into 1 g. of the  $\beta$ - and 3-5 g. of the  $\gamma$ -form. The  $\beta$ -form, long slender prisms from alc., sublims perceptibly at  $100^\circ$  *in vacuo*,  $[\alpha]_D^{18}$   $45.73^\circ$  in  $(CHCl_3)_2$ ;  $\gamma$ -form, m.  $83-5^\circ$ ,  $[\alpha]_D^{18}$   $28.05^\circ$ . The  $\beta$ -form (5 g.) shaken until dissolved (10 min.) with 50 cc. MeOH satd. at  $0^\circ$  with  $NH_3$  and allowed to stand 3 hrs. at  $15-20^\circ$  gives 2.3 g.  $\beta$ -methylramnoside, long felted needles from AcOEt, m.  $138-40^\circ$ ,  $[\alpha]_D^{20}$   $95.39^\circ$  ( $H_2O$ ), mol. wt. in PhOH  $193^\circ$ , does not reduce Fehling soln. even on long heating, is not decompd. by emulsin or brewer's yeast but is hydrolyzed by heating 1 hr. at  $100^\circ$  with 0.1 N HCl. The  $\gamma$ -triacetate, however, with alkalis or  $Ba(OH)_2$ , even on heating, loses only 2 mols. AcOH; 2 g. allowed to stand 12 hrs. at  $20^\circ$  in 25 cc. MeOH satd. at  $0^\circ$  with  $NH_3$  yields 1.1 g.  $\gamma$ -methylramnoside monoacetate, prismatic needles from AcOEt,  $[\alpha]_D^{14}$   $16.3^\circ$  ( $H_2O$ ), mol. wt. in PhOH  $209$ , m.  $143-4^\circ$ , does not reduce Fehling soln. even on long boiling but is very sensitive towards hot acids, even when very dil., 0.1 g. being quant. hydrolyzed by heating 30 min. with 1 cc. of 0.01 N HCl. If the alc. mother liquors from the mixt. of the  $\beta$ - and  $\gamma$ -triacetates are evapd. *in vacuo*, taken up in  $Et_2O$ , freed from the last traces of Ag compds. with charcoal and again evapd. *in vacuo* there is obtained a thick sirup which is freed from the small amt. of reducing substances still present by distg. 4-5 times under 0.2 mm. at about  $150^\circ$ , care being taken to interrupt the distn. each time when about 0.9 has passed over. The resulting  $\delta$ -triacetate is a colorless or at most very faintly yellow sirup which hardly reduces Fehling soln.,  $[\alpha]_D$   $32.2-4.2^\circ$  in  $(CHCl_3)_2$ , gives on hydrolysis with  $Ba(OH)_2$  and subsequent removal of the Ba with  $H_2SO_4$  a sirupy methylramnoside which, when fresh, usually contains about 10% of reducing substances and on long standing gradually decomp. into rhamnose, mol. wt. in PhOH  $184-200$ , is completely hydrolyzed by heating 1 hr. at  $100^\circ$  with 10 parts of 0.1 N HCl. From 10 g. A, 4.4 g. quinoline and 10 cc. MeOH allowed to stand 1.5 hrs., then shaken with  $Ag_2CO_3$ , filtered, evapd. *in vacuo* repeatedly treated with  $H_2O$ , again evapd. *in vacuo* and crystd. from  $EtOH-H_2O$  is obtained 20-40% of the  $\gamma$ -triacetate.  $\alpha$ -Triacetate, from B (Ber. 28, 1158) with  $C_6H_5N$  and  $Ac_2O$  (yield, 73%), slender leaflets from 50% alc., m.  $86-7^\circ$ ,  $[\alpha]_D^{18}$   $-53.66^\circ$  ( $CHCl_3$ ). A (5 g.) and 9 g. menthol shaken 2 hrs. with 5 g.  $Ag_2CO_3$  in 50 cc.  $Et_2O$

filtered, freed from Et<sub>2</sub>O and menthol with steam as quickly as possible, quickly cooled, sepd. from the supernatant liquid by decantation, dried, dissolved in 10 cc. ligroin and cooled to 0° gives 1.3 g. of  $\alpha$ -l-menthylrhamnoside diacetate, slender needles from 50%, alc., m. 134-5°,  $[\alpha]_D^{15}$  13.3° (alc.), becomes strongly electrified on rubbing, does not reduce Fehling soln. The mother liquors on evapn. and distn. at 180-90° under 0.25 mm. yield another menthyl rhamnoside acetate, possibly not entirely homogeneous, as a faintly yellow sirup.  $\alpha$ -l-Menthyl rhamnoside, from 5 g. of the cryst. diacetate in 100 cc. MeOH satd. at 0° with NH<sub>3</sub> and allowed to stand 5 hrs. at 20°, evapd. *in vacuo* and treated with warm H<sub>2</sub>O (yield, 3.5 g.), microprisms from Me<sub>2</sub>CO-H<sub>2</sub>O, m. 114-5°,  $[\alpha]_D^{20}$  -7.48° (alc.), does not reduce Fehling soln., tastes very bitter.  $\beta$ -Isomer (2.5 g. from 5 g. of the oily acetate), microplates with 0.5 H<sub>2</sub>O from 50% alc., m. 184-6°,  $[\alpha]_D^{21}$  -130.70°, mol. wt. in PhOH 297, gradually develops a long continued bitter taste on the tongue, does not reduce Fehling soln. even on boiling, is hydrolyzed more slowly than the  $\alpha$ -compd. by HCl.

C. A. ROUILLER

**Halogenation. XX.** The replacement of sulfonic acid groups by halogens. RASIK LAL DATTA AND JAGADISH CHANDRA BHOUMIK. *J. Am. Chem. Soc.* 43, 303-15(1921); cf. C. A. 14, 182.—A continuation of the earlier work has shown that the replacement of SO<sub>3</sub>H groups in aromatic compds. occurs generally with Cl and Br and may occur with I under special conditions; it frequently happens that not only does the halogen replace the SO<sub>3</sub>H group but more halogens usually enter the ring with the formation of polyhalogen derivs. This process possesses over the ordinary halogenation methods the advantages that there is no charring and in most cases gives a satisfactory yield of the pure halogen deriv.; by its means may also be prepd. many halogen derivs. which before could not be obtained. Substituents already present in the nucleus exert a great influence upon the replacement. The replacement by Br takes place readily at room temp. in compds. with one or more HO groups on the nucleus, also in those with an NH<sub>2</sub> group. NO<sub>2</sub> groups, on the other hand, retard the replacement, although even in these cases the yields are good. In hydroxycarboxylic acids the SO<sub>3</sub>H group is replaced by halogen but at the same time the CO<sub>2</sub>H group is split off. Halogens already present on the nucleus hinder the replacement still more. One or more alkyl groups likewise render the replacement difficult. In the absence of any substituents at all (PhSO<sub>3</sub>H) there is no replacement at all. A mixt. of alkali bromide and bromate reacts better than free Br, as the Br is liberated very gradually with simultaneous substitution, eliminating entirely the chances of charring and secondary reactions; moreover, such a mixt. is more reactive than free Br alone. A mixt. of chloride and chlorate gives no better results than free Cl, but an iodide and an iodate, again, react better than free I. The replacement occurs more readily in mono- than in di- and trisulfonic acids. In the following expts., unless otherwise stated, the substance to be halogenated was employed in the form of an aq. soln. of the sulfonation product obtained by heating it with H<sub>2</sub>SO<sub>4</sub>. From PhOH (as HOC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H) with liquid Br is obtained 2,4,6-Br<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH quant.; from *m*-cresol 3,2,4,6-MeBr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH quant.; from *p*-cresol, 4,2,3,5-MeBr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH in 90% yield; from 2,4-xyleneol, 3,6-dibromo-2,4-xyleneol quant., crystals from AcOH, m. 106°, insol. in H<sub>2</sub>O but partially decompd. in contact with it, giving it a red tint, loses part of its Br when heated with alc.; from 3,4-xyleneol, 3,4,2,5,6-Me<sub>2</sub>-Br<sub>2</sub>C<sub>6</sub>OH quant.; from carvacrol, 3,5-dibromocarvacrol; from thymol, 2,6-dibromothymol; from *m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, 1,3,2,4,6-C<sub>6</sub>H<sub>2</sub>(OH)<sub>2</sub>Br<sub>2</sub> quant.; from quinol, 1,4,2,3,5-C<sub>6</sub>H<sub>2</sub>(OH)<sub>2</sub>Br<sub>2</sub>; from 4 g. orcinol, about 15 g. 2,2,4,4,6-pentabromorcinol; from PhOEt, 50% of 2,4,6-Br<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OEt; from *o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OH, 50% of 4,6,2-Br<sub>3</sub>(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH; from 2 g. *m*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OH, 5 g. of 2,4,6,3-Br<sub>3</sub>(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH; from *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OH, 90% of 2,6,4-Br<sub>3</sub>(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH; from 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH, 50% of 6,2,4-Br<sub>3</sub>(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH; from PhNH<sub>2</sub>, 2,4,6-Br<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NH<sub>2</sub> almost quant.; from *m*-toluidine, 60% of 3,2,4,6-MeBr<sub>3</sub>-

$C_6H_5NH_2$ , from  $o$ - $O_2NC_6H_4NH_2$ , 70% of 4,6,8- $Br_3(O_2N)C_6H_4NH_2$ ; from 1 g.  $m$ - $O_2NC_6H_4NH_2$ , 2 g. 2,4,6,8- $Br_3(O_2N)C_6H_4NH_2$ ; from  $p$ - $O_2NC_6H_4NH_2$ , 2,6,8- $Br_3(O_2N)C_6H_4NH_2$  almost quant.; from  $o$ - and  $p$ - $HOC_6H_4CO_2H$ , 2,4,6- $Br_3C_6H_3OH$  almost quant.; from 2,4-( $HO$ ) $_2C_6H_3CO_2H$ , 40% of 1,3,2,4,6- $C_6H_3(OH)_3Br_3$ ; from  $PhBr$  (1 g. of  $p$ - $BrC_6H_4SO_3H$ ), 2 g. 1,2,4,5- $C_6H_3Br_3$ ; from  $PhMe$ , 40% of 2,4,5- $Br_3C_6H_3Me$ ; from  $m$ -xylene heated with an excess of  $Br$  on the  $H_2O$  bath, a little 1,3,4,6- $C_6H_3Me_3Br_3$ , and when allowed to stand 3 days with excess of  $Br$ , 40% of 1,3,2,4,5,6- $C_6Me_3Br_3$ ; from  $p$ -xylene, 50% of 1,4,2,5- $C_6H_3Me_3Br_3$ ; from mesitylene, 50% 1,3,5,2,4,6- $C_6Me_3Br_3$ ; from  $Ph_3$ , 13% of ( $p$ - $BrC_6H_4$ ) $_3$ . Catecholsulfonic acid gives no definite product with  $Cl$  in  $H_2O$ , but in  $AcOH$  it gives a good yield of tetrachloro- $o$ -quinone; quinsulfonic acid in  $AcOH$  yields tetrachloro- $p$ -quinone; 2,4-xylenolsulfonic in  $H_2O$  gives a little of a dichloro-2,4-xenol, b.  $232^\circ$ ; 4,2-xenol (in the original the two xylenols are given as 1,2,4 and 1,4,2, so possibly these are the 3,4- and 2,5- $Me_2C_6H_3OH$ .—ABSTRACTOR) gives a dichloroxyenol, needles, m.  $84^\circ$ ;  $PhBr$  gives  $p$ - $ClC_6H_4Br$  almost quant.;  $p$ -xylene yields 1,4,2,5- $C_6H_3Me_3Cl_3$ ; mesitylene gives 1,3,5,2,4,6- $C_6Me_3Cl_3$ . Mesitylenesulfonic acid in  $H_2O$  with  $KIO_4$  and then  $KI$  gives iodomesitylene.

C. A. ROUILLER

The structures and reactions of hydroxylamine and its derivatives. ARTHUR MICHAEL. *J. Am. Chem. Soc.* 43, 315–32(1921).—M. discusses the evidence, especially the work of Jones (*C. A.* 8, 2698), that hydroxylamine ( $A$ ) and its derivs. behave tautomerically. He concludes that all the properties of  $A$ , its derivs. and salts can be satisfactorily explained only by the  $HO$  structure,  $NH_2OH$ , and that there is no indication of their existence in tautomeric amine oxide forms which, for energy and affinity reasons, under ordinary conditions should represent labile substances. The chem. resemblance between  $A$  and  $H_2O_2$  is superficial and without value in establishing the structure of the base. There is no theoretical or expl. evidence for the existence of  $A$ , its salts and derivs. and hydroxylammonium products in "electromeric" modifications and the "electronic" explanations of the reactions of these compds. are not tenable.  $A$ , its alkyl derivs. and the trialkylamine derivs. are not oxidizing agents in the accepted sense of the term and there is no reason for supposing that the hypothetical  $H_2NO$  would act as such a reagent. The property is somewhat more developed in the salts with strong acids, owing to the increase in affinity between the  $N$  and the hydroxyl  $O$  with the increase in the free negative chem. energy accompanying salt formation and the possibility of a large increase in entropy with the generation of the corresponding ammonium salt. All inter- and intramol. condensations occurring in org. compds. with loss of  $H_2O$  or  $NH_3$  and involving a  $CO$  or  $NO$  group, proceed in the first phase through an enolization or an aldolization of these radicals. The direct formation of  $H_2O$  or  $NH_3$  by the union of a carbonyl or nitrosyl  $O$  with several  $H$  atoms is energetically impossible, for the affinity and free chem. energy conditions reside in these  $O$  atoms, which are necessary to overcome the chem. hindrance to the change, i. e., the bound chem. energy between the migrating  $H$  and the atoms to which it is joined. Reversely,  $H_2O$ ,  $NH_3$  or other addenda with more than one available  $H$  always function by sepg. into a single  $H$  and the remaining radical.

CHAS. A. ROUILLER

Phototropism in solution. I. BAWA KARTAR SINGH. *J. Am. Chem. Soc.* 43, 333–4(1921).—With one possible exception, di-9-hydroxyphenylanthryl-10-amine (Forrest, *C. A.* 9, 1474), phototropy has hitherto been observed only in the case of solids. The colorless soln. of  $\alpha$ -naphthylaminocamphor ( $A$ ) in  $CHCl_3$  remains so in the dark but in direct sunlight becomes deep bottle-green within 1 min. The same is true of  $m$ -phenylenetetrakisaminocamphor exposed to direct sunlight about 5 min. Again, the slightly reddish soln. of  $\alpha$ -tetrahydro- $\alpha$ -naphthylaminocamphor in  $CHCl_3$  becomes green in about 2 min. in sunlight. The green color in the above solns. completely disappears after about 24 hrs. in the dark. The time required for the change from the color-

less to the colored solns. varies considerably with the intensity of the light; electric light and the Na flame have no effect on the colorless solns. Senior and Shephard's explanation that the change is due to extra-mol. rearrangement into mol. aggregates (C. A. 4, 1025) may be quite applicable to solid substances but is untenable in the case of solns. in which the change is very probably due to a change in the chem. structure of the mol. Thus, in the case of A, the change may be represented as being of the keto-enol type, the green color being due to the enol form. The imino compds. in the 3 above cases do not show phototropic behavior; this is produced only when the imino is transformed into the amino compd., in which case alone the tautomeric change is possible.

CHAS. A. ROUILLER

Condensation of acetylene with benzene and its derivatives in the presence of aluminium chloride. OTTO W. COOK AND VICTOR J. CHAMBERS. *J. Am. Chem. Soc.* 43, 334-40(1921); cf. Varet and Vienne, *Compt. rend.* 164, 1375(1886).—V. and V.'s expts. were duplicated as closely as possible and in attempts to modify the reaction there were substituted for  $C_6H_6$  some of its derivs. In all case the yields were low and variable, the only influence of the substituted groups being to vary the intensity of the reaction as a whole rather than to produce any change in the nature or relative amts. of the products. The normal course of the reaction is the union of 2 mols. of  $C_6H_6$  with one of  $C_2H_2$  to form a diphenylethane and a combination of a part of this with more  $C_2H_2$  to produce an anthracene. The formation of a styrene from 1 mol. each of  $C_6H_6$  and  $C_2H_2$  either takes place to only a slight extent or, more probably, the unsatn. of the compd. formed leads to its immediate condensation with another mol. of  $C_6H_6$  and the formation of the diphenylethane. Freshly prepd. nearly pure  $AlCl_3$  was found to be much too active, but after it had stood 2 weeks to 6 months in sealed bottles, almost any desired intensity of reaction could be obtained with it. With  $C_6H_6$  were obtained, besides a small amt. of material b. 140-5° and giving evidence of the presence of styrene, Ph·CHMe and 9,10-dimethylantracene hydride; C. and C. cannot account for the large amt. of styrene reported by V. and V. From the results of a large number of runs it is concluded that the fresher the  $AlCl_3$  the greater is the proportion of anthracene formed; the rate of flow of  $C_2H_2$  has little effect on the proportions of the products; diln. of the  $C_6H_6$  with a neutral solvent has no appreciable effect. PhMe yielded (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>·CHMe, a mixt. of anthracenes, identified by oxidation to the anthraquinones as 2,7-dimethylantracene (a small amt. of which, m. 243.5°, was isolated), β-methylantracene and 1,6-dimethylantracene, and xylene, mesitylene and pseudocumene. With PhCl were obtained unsym-*p,p*-dichlorodiphenylethane, b<sub>20</sub> 210-2°, b. 319-21°, and a higher boiling product not yet identified. PhNO<sub>2</sub> does not condense with  $C_2H_2$  and  $AlCl_3$ . PhOH, BzOMe and PhNH<sub>2</sub> unite with the  $AlCl_3$  in mol. proportions and do not react further. PhNMe<sub>2</sub> gives a small amt. of (*p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>·CHMe. AcOPh rearranges into *p*-HOCH<sub>2</sub>·COMe.

CHAS. A. ROUILLER

Derivatives of 2,4,6-trinitrobenzaldehyde. ALEXANDER LOWY AND EMIL HAROLD BALZ. *J. Am. Chem. Soc.* 43, 341-6(1921).—By a modification of the Sachs and Kempf method (cf. also Everding, *Ber.* 36, 960(1903)) the yield of 2,4,6-(O<sub>2</sub>N)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>·CHO (A) was increased to 60%. The following addition products were prepd. by treating A in boiling alc. containing some H<sub>2</sub>O with 1 mol. of the amine; aniline, A. PhNH<sub>2</sub>, red plates, m. 86°; *o*-toluidine, reddish, m. 106°; β-naphthylamine, reddish brown; α-isomer, reddish brown; diphenylamine, reddish, m. 102°. When treated with glacial AcOH or heated they lose H<sub>2</sub>O and form the anils; *o*-toluidine, yellow, m. 177°; β-naphthylamine, yellow, m. 192°; α-isomer, orange, m. 242°; *p*-toluidine, yellow, m. 179.5°; 1,3,4-xylidine, yellow, m. 203°; *p*-aminoazobenzene, brick-red, m. 189°; *p*-aminophenol, yellow, m. 179°; *o*-aminobenzoic acid, brick-red, m. 146°; *m*-toluidine, yellow, m.

173.5°. In dil. aq. alc. the tendency is for the addition products to form while in abs. alc. or glacial AcOH the condensation products are usually obtained directly. Steric hindrance seems to exert a considerable influence on the condensation (cf. Spaeth, *C. A.* 5, 864); sulfanilic acid does not condense while its Na salt does. In alc. A gives with  $\text{PhNH}_2$  Sachs and Everding's anil, m. 162° (*Ber.* 36, 960(1903)) but in glacial AcOH is obtained a light yellow isomer, m. 220° (decompn.). In certain cases the addition products, when dried, undergo change in either direction, i. e., into the components or into  $\text{H}_2\text{O}$  and the anil. Further exptl. work is being done on the identification of the theoretically possible optical isomers of the addition products and the *syn*- and *anti*-isomers of the anils.

CHAS. A. ROULLER

**Derivatives of 2,4-dinitrobenzaldehyde. II.** ALEXANDER LOWY AND THOMAS B. DOWNHY. *J. Am. Chem. Soc.* 43, 346-8(1921); cf. *C. A.* 14, 1828.—The following 2,4-dinitrobenzal compounds were prepd. from 2,4-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{CHO}$  and 1 mol. of the amine in alc. (except the 2nd and 3rd, which were prepd. in AcOH); all sep. in yellow or orange needles (the % yields are given in parentheses); *p*-bromoaniline, m. 162.5° (90); 2,4,6-tribromoaniline, m. 185° (80); *o*-nitroaniline, m. 174.5° (89); *m*-isomer, m. 138° (92); *p*-compound, m. 169.5° (95); *o*-phenetidine, m. 141.5° (94); *o*-anisidine, m. 140° (89); *p*-isomer, m. 129° (90). All are considerably affected by light, especially those containing halogen; 2,4,6- $\text{Br}_3\text{C}_6\text{H}_2\text{NH}_2$  does not condense with the aldehyde in 95% alc. after 6 hrs. heating but in glacial AcOH condensation takes place in 3 hrs.

CHAS. A. ROULLER

**Preparation of some alkyl derivatives of resorcinol and the relation of their structure to antiseptic properties.** TREAT B. JOHNSON AND FREDERICK W. LANE. *J. Am. Chem. Soc.* 43, 348-60(1921).—Although it is well understood that the substitution of one or more Me groups into the nucleus of PhOH increases the germicidal value and lowers the toxicity, nothing appears to be known as to how the antiseptic strength would be affected by replacing the Me group by other alkyl radicals, a phase of the subject in which J. and L. are especially interested. Inasmuch as PhOH and many of its derivs. are rather highly toxic, they have chosen the less poisonous *m*- $\text{C}_6\text{H}_4(\text{OH})_2$  (A) as their starting point or standard phenol and have detd. the "phenol coeffs." of the Me, Et, Pr and Bu homologs in which the alkyl group is in position 4 (the two HO groups being in 1 and 3). 2,4-(HO) $_2\text{C}_6\text{H}_3\text{CHO}$  (A) can be obtained in 40% yield by Dimroth and Zoepf's method (*Ber.* 35, 994(1902)) when the amt. of alkali which they recommend for the hydrolysis of the intermediate Schiff base is increased. Karrer's method (*C. A.* 13, 960) gave only 13-21% yields of a product m. 120-9°. Gattermann's method (*Ber.* 32, 278(1899)), so modified that the HCN can be used in gaseous instead of liquid form, gives very satisfactory results. A is reduced by Clemmensen's method (*C. A.* 8, 1112) to methylresorcinol (B), characterized by its widely varying m. p. (70-104°), depending upon the solvent and the number of crystns., an experience shared by previous investigators. The obvious explanation would seem to be that the B is contaminated with its isomers, although all attempts to isolate such impurities by fractional crystn. failed. If one or both of the isomers of B is present, the accepted formula for A must be incorrect or there is a partial rearrangement during the reaction. 2,4-(HO) $_2\text{C}_6\text{H}_3\text{COMe}$ , obtained in 57% yield by Nencki and Sieber's method (*J. prakt. Chem.* 23, 147(1881)), is smoothly and nearly quant. reduced to 2,4-(HO) $_2\text{C}_6\text{H}_3\text{Et}$  (C). 2,4-(HO) $_2\text{C}_6\text{H}_3\text{COEt}$ , obtained in 86% yield from A,  $\text{EtCO}_2\text{H}$  and  $\text{ZnCl}_2$ , gives more than 60% (HO) $_2\text{C}_6\text{H}_3\text{Pr}$  (D). Butylresorcinol, obtained in 76% yield from A,  $\text{PrCO}_2\text{H}$  and  $\text{ZnCl}_2$ , crystals from  $\text{CCl}_4\text{-C}_6\text{H}_6$  (3:1), m. 69-70° *oxime*, crystals from  $\text{EtOH}$ ,  $\text{CHCl}_3$  or  $\text{C}_6\text{H}_6$ , m. 189-90°. On reduction the ketone gives 78% of butylresorcinol (E), b<sub>p</sub> 155-75°. The "phenol coeffs." of the above compds. were found to

be as follows: A 0.8, C 1.5, D 4.3, E 8.0; the antiseptic properties are, therefore, very definitely detd. by the length or wt. of the hydrocarbon side chain introduced into the A. C. A. R.

**New benzyl esters possessing an antispasmodic action.** H. A. SHONLE AND P. Q. ROW. *J. Am. Chem. Soc.* 43, 361-5 (1921).—In view of the fact that many benzyl derivs. have been found to possess antispasmodic properties (Macht, *C. A.* 13, 44), a number of  $\text{PhCH}_2$  esters have been prepd. and their physical properties and therapeutic activity detd. The esters of the satd. higher fatty acids are tasteless odorless liquids or low melting solids; those of both the satd. and unsatd. higher fatty acids are insol. in  $\text{H}_2\text{O}$  but readily sol. in  $\text{CHCl}_3$ ,  $\text{Et}_2\text{O}$  and  $\text{C}_6\text{H}_6$ , somewhat less sol. in alc., olive oil and petr. oil. The slight but distinct local anesthetic effect noticeable in the lower esters, as well as their irritating action on the mucous membrane, is absent in the higher esters, owing presumably to their low soly. Because of this insoly. the usual physiol. tests on animals or on excized tissues were not entirely satisfactory as a means of estimating their relative activity on smooth muscle structure. Clinical tests, however, demonstrated their antispasmodic action in asthma, dysmenorrhea, high blood pressure, pylorospasm and spastic constipation. While they are very resistant to hydrolysis by steam, they are readily hydrolyzed by lipase (the  $\text{PhCH}_2$  ester of com. stearic acid was hydrolyzed to the same extent as the olive oil used as control). When the aliphatic acids are replaced by aromatic acids there is a very marked reduction in the rate of hydrolysis. The *p*- and *m*-aminobenzoates, on account of the insoly. of their  $\text{HCl}$  salts and of their irritating effect on mucous membrane, were not tested for antispasmodic action. Both have local anesthetic properties. The lactate, on account of its irritating effect, was not tested clinically. The esters of the individual fatty acids have nothing to recommend their therapeutic use over that of the esters of mixts. of acids derived from natural sources; if these mixts. contain any considerable amts. of unsatd. acids, however, the resulting esters are colored and have an unpleasant taste. The following benzyl esters were made from the acid chloride (prepd. with  $\text{PCl}_5$  or better with  $\text{SOCl}_2$ ) in  $\text{Et}_2\text{O}$  and  $\text{PhCH}_2\text{OH}$ : *laurate*,  $b_{12}$  209–11°,  $m$  8.5°,  $d_{25}^{25}$  0.9457,  $n_{20}$  1.4812; *myristate*,  $b_{11}$  229–31°,  $m$  20.5°,  $d_{25}^{25}$  0.9321,  $n_{20}$  1.4803; *palmitate*,  $m$  36.0°,  $d_{25}^{25}$  0.9136,  $n_{20}$  1.4689; *stearate*,  $m$  45.8°,  $d_{25}^{25}$  0.9075,  $n_{20}$  1.4663; *oleate*,  $b_7$  237°,  $d_{25}^{25}$  0.9330,  $n_{20}$  1.4875; *lactate*, from the alc. and lactic acid (dehydrated at 180°) heated 10–2 hrs. at 220–30° with  $\text{HCl}$  as catalyst,  $b_{7-8}$  128–30°,  $n_{20}$  1.5252. *p*-Aminobenzoate, from the *nitro* ester,  $m$  84.7°, by reduction with  $\text{Sn}$  and alc.  $\text{HCl}$  or by powdered  $\text{Fe}$  and  $\text{HCl}$ , is a yellow viscous liquid becoming wax-like on standing; *hydrochloride*,  $m$  184° (slight gas evolution); *m*-aminobenzoate, dark liquid forming a cryst. *hydrochloride*, is obtained from the *nitro* ester, light yellow liquid,  $b$  308°. No  $\text{PhCH}_2$  ester of  $o$ - $\text{HO}_2\text{SC}_6\text{H}_4\text{CO}_2\text{H}$  or glyccol could be obtained. The esters of the higher fatty acids can be made in large amt. by the action of  $\text{PhCH}_2\text{Cl}$  on the anhydrous alkali salt of the acid dissolved in an excess of that acid at 170–80°. CHAS. A. ROULLIER.

**Indirect reduction of 3-amino-4-hydroxyphenylarsonic acid to arspenamine.** WALTER G. CHRISTIANSEN. *J. Am. Chem. Soc.* 43, 370-5 (1921); cf. *C. A.* 15, 675. —The arspenamine (A) of low toxicity prepd. by reduction of 4,3-HO( $\text{H}_2\text{N}$ ) $\text{C}_6\text{H}_3\text{AsO}_2\text{H}_2$  (B) with  $\text{H}_3\text{PO}_2$ , as described in the earlier paper, dissolves easily in  $\text{H}_2\text{O}$  only on warming to 55°. It has now been found that if the B in  $\text{HCl}$  is reduced to the arsenious oxide (C) with  $\text{KI}$  and  $\text{SO}_2$ , the  $\text{SO}_2$  is removed by aeration and the resulting soln. is reduced with  $\text{H}_3\text{PO}_2$  there is obtained 86.5% of A as a slightly orange-yellow ppt. readily sol. in  $\text{H}_2\text{O}$  and relatively non-toxic (tolerated dose, 130–40 mg./kg.). The removal and the method of removal of the  $\text{SO}_2$  is of great importance. If it is not removed the addition of the  $\text{H}_3\text{PO}_2$  results in the production of  $\text{H}_2\text{S}$  and the pptn. of S. If it is expelled by boiling the C decomps. and when the  $\text{H}_3\text{PO}_2$  is added a small

amt. of polyarsenide (D) of A is obtained instead of A. Addition of  $\text{Na}_3\text{AsO}_3$  to the aerated C soln. produces the same D (contrary to the statements in the literature this D is not more toxic than A (the tolerated dose is 140 mg./kg.), hence it is improbable that it is a factor in the toxicity of com. preps. of A). When B is reduced in HCl with KI and  $\text{SO}_2$ , freed from the  $\text{SO}_2$  by aeration and boiled 55 min., it gives an immediate yellow ppt. with  $\text{H}_2\text{S}$  (inorg. As; a control aerated but not boiled soln. gave no such ppt.) and on neutralization with  $\text{Na}_2\text{CO}_3$  yields a curdy ppt. of 3,3'-diamino-4,4'-dihydroxydiphenylarsenious oxide,  $([\text{HO}(\text{H}_2\text{N})\text{C}_6\text{H}_3]_2\text{As})_2\text{O}$ , which is reduced by  $\text{H}_2\text{PO}_3$  to 3,3',3'',3'''-tetraamino-4,4',4'',4'''-tetrahydroxytetraphenyldiarsine tetrahydrochloride, a flaky white solid. If the soln. of reduced B, after aeration, is refluxed 4.5 hrs., the final product is  $o\text{-H}_2\text{NC}_6\text{H}_4\text{OH}$ . To det. the rate at which C decomps. advantage was taken of the fact that as the quantity of inorg. As increases the color produced on addition of  $\text{H}_2\text{PO}_3$  changes from the bright yellow of A solns. to the deep red of the D solns.; when 50% of the C has been decompd. the max. amt. of D will be formed and from this point on there will be an excess of inorg. As and on reduction with the  $\text{H}_2\text{PO}_3$  a mixt. of D and metallic As is formed, the soln. becoming paler and paler and the ppt. darker and darker as the amt. of As increases. In this way it was found that the decompn. of C in boiling acid is at first very rapid (50% in 40 min.) and then becomes slower (75% after 3 hrs.)

CHAS. A. ROULLER

**5-Nitro-4-hydroxy-3-methylbenzoic acid.** K. PFISTER. *J. Am. Chem. Soc.* **43**, 375-6(1921).—The compd. obtained by Mahon by nitrating 3,4-Me(HO) $\text{C}_6\text{H}_3\text{COOH}$  (A) at a high temp., supposed by him to be 5-nitro-4-hydroxy-3-methylbenzoic acid (B) (*Am. Chem. J.* **4**, 1887(1882)) and so listed in Beilstein and in Richter's "Lexikon" is really 2,4,6-Me(O $_2$ N) $_2\text{C}_6\text{H}_2\text{OH}$ . The true B, obtained nearly quant. by nitrating A with mixed acid with the usual precautions, seps. from AcOH or  $\text{C}_6\text{H}_6$  in pale lemon-yellow needles, m. 240°. *Methyl ester*, lemon-yellow crystals, m. 103°; *aminoester*, m. 141°.

C. A. R.

**Aristol.** G. H. WOOLLEY. *J. Am. Chem. Soc.* **43**, 553-61(1921); cf. C. A. **15**, 680.—In the study of Lautemann's red (A), a supposed analog of aristol (B), described in the earlier paper, certain facts were discovered which did not agree with the data on B. The present work was undertaken to substantiate that on A and to straighten out, if possible, the chemistry of B. It was found that B is not homogeneous and can be sepd. by extn. with cold alc. into a sol. brown tarry fraction (about 40%) and an insol. colorless or faintly yellow fraction. No cryst. substance other than a small amt. of I could be obtained from the sol. fraction; this fraction produced more B with alkali if the free I was not removed first. By varying the proportions of I, thymol and alkali but otherwise proceeding as in the prepn. of B, different results were obtained; with 1 equiv. of each iodothymol was formed; with 1 equiv. of thymol and 2 of the others there was obtained a gum almost completely sol. in alc. and acting in every way like the sol. fraction of B; 1 equiv. of thymol and 4 of alkali and I gave B. Iodothymol with 1 equiv. each of I and alkali gave the sol. gum; with 2 equivs., B. The insol. fraction of B resembles leuco-A and can be oxidized to a red substance looking like fresh A and B but not at all sol. in alc.; the reoxidized insol. fraction retains its color much longer than fresh B and also gives off less I. The insol. fraction of B shows no tendency to adsorb I. The presence of the sol. fraction or some similar substance is necessary for the rapid loss of color and production of I by B; the change taking place during this reaction was found to be an oxidation of the sol. by the insol. part. Iodothymol alone gives up no I under similar conditions but a mixt. with A acts in every way like the re-oxidized insol. fraction; as the production of I progresses the red color becomes fainter. The mol. wt. of the insol. fraction in freezing  $\text{C}_6\text{H}_6$  ranges from 1940 to 2268, in thymol from 1280 to 1360; after oxidation, from 3670 to 4430 in  $\text{C}_6\text{H}_6$ , these high values substantiating the



view that the red part of **B** is analogous to **A**. The lower values in thymol may be due to dissociation or, not improbably, to reaction between the solvent and solute. The **I** content of the insol. fraction, both before and after oxidation, was never equal to that required by the formula  $(C_{10}H_{11}OI)_n$ .

CHAS. A. ROUILLER

The purification and some physical properties of certain aliphatic alcohols. ROGER F. BRUNEL, J. L. CRENSHAW AND ELISE TOBIN. *J. Am. Soc.* **43**, 561-77(1921).—A series of aliphatic alcs. containing, if possible, not more than 0.1-0.2% impurity being needed by the authors they have undertaken to purify them by a somewhat more careful fractionation than is usually carried out. As the chief criterion of the purity of their products is in the data obtained in the distn., they describe in some detail the app. and the various fractions obtained. The most distinctive feature of the app. is the still head which usually consisted of brass tubes 1.8 m. tall and 30 mm. in diam. filled with quartz pebbles passing through a 4- but not a 5-mesh wire net. The products were considered as "const. boiling" when they boiled within 0.01°, as nearly as the thermometer could be read, and the chief criterion of purity was the extent to which a const. boiling fraction finally again comes over at const. temp. The exact b. ps. of the products were detd. in a specially designed app. with a thermo-element. The most persistent difficulty which had to be overcome was the fall in b. p. always occurring with the higher boiling alcs. when the violence of the boiling was increased and which was found to be due to incomplete drying of the alcs. The question of the action of drying agents was, therefore, given special consideration. Na is not satisfactory; lime gives good results; Ca acts more rapidly than lime but in the one case tried did not give a product of const. b. p.; BaO acts more rapidly but no more efficiently than lime; Al-Hg was found to be very effective. Below are given, resp., (1) the % of the distillate which boiled const.; (2)  $dl/dP$  deduced from the authors' own detns. of the b. ps. on different days; (3) the b. p. calcd. for 760 mm.; (4)  $d_4^{25}$ ; (5)  $n_D^{25}$ . The last 4, which are "most probable values," are not always the mean of the results but are based upon the authors' judgment as to the relative values of the tests and the purities of the specimens. EtOH, 100, 0.035, 78.32°, 0.78505, 1.3595; PrOH, 78, 0.036, 97.19°, 0.7998, 1.3833; *iso*-PrOH, 87, 0.033, 82.26°, 0.7808, 1.3749; BuOH, 90, 0.036, 117.71°, 0.8057, 1.3974; *iso*-BuOH, 73, 0.036, 107.89°, 0.79801, 1.3939; *sec*-BuOH, 97, 0.036, 99.53°, 0.80271, 1.39495; *iso*-BuCHMeOH 96, 0.040, 131.82°, 0.8025, 1.40895. A table of the consts. detd. by other workers is appended.

CHAS. A. ROUILLER

Nitrotartaric acid. ARTHUR LACHMAN. *J. Am. Chem. Soc.* **43**, 577-81(1921).—Nitrotartaric acid (**A**) can be obtained in 60-75% yield without the use of fuming  $HNO_3$ , as was done by Dessaignes (*Compt. rend.* **54**, 731(1862)), by adding 50 g. powdered tartaric acid (**B**) to 70 cc.  $HNO_3$  (d. 1.42), then 200-50 cc. concd.  $H_2SO_4$  and allowing to cool slowly for several hrs. Although it reacts violently with alkalis, it is unexpectedly stable towards  $Na_2CO_3$  with which it titrates sharply (Me orange) at 0° as a dibasic acid. When it is dried in  $Et_2O$  with  $CaCl_2$  there is gradually formed a mixt. of the Ca salts of **A** and dihydroxytartaric acid (**C**) and the  $Et_2O$  is found to contain  $NOCl$ . Careful evapn. of a concd. soln. of **A** in  $Na_2CO_3$  yields an impure solid Na salt, extremely sol. in  $H_2O$ . Moist **A** decomps. with some violence well below 100° but when perfectly dry can be heated to the b. p. of xylene without change. Aq. solns. of **A** on standing soon become blue, evolve heat and give off gases, at first  $N_2O_5$ , then  $NO + CO_2$ ; they now contain chiefly **C** (pptd. by  $NaOAc$  or  $Na_2CO_3$  as the Na salt; yield, 75-80%), tartronic and oxalic acids, but little or no **B** (the highest amt. found in many different hydrolyses was 1.3%). The tartronic acid results from the decomp. of the **C** and the  $(CO_2H)_2$  from the oxidation of the tartronic acid by  $HNO_3$ . When **A** is neutralized with  $NaOH$  much heat is evolved, and, regardless of diln. within ordinary limits, cooling to -5° or using alc. as solvent,  $NaNO_2$  is formed practically quant. and the **C** is

completely decompd., with formation of tartronic acid and considerable  $(\text{CO}_2\text{H})_2$ . The same results are obtained with  $\text{Ca}(\text{OH})_2$ . Solid A moistened with a little  $\text{H}_2\text{O}$ , especially in the presence of strong acids, decomp. into  $\text{HNO}_3$  and B, and in this form is, therefore, a true  $\text{HNO}_3$  ester of B, but in  $\text{H}_2\text{O}$  and with alkalis it behaves like the nitrite of C. The best explanation of these facts is that A rearranges into a pseudo form;  $[\text{HO}_2\text{CCH}(\text{ONO}_2)]_2 \longrightarrow [\text{HO}_2\text{CC}(\text{OH})(\text{ONO})]_2$ , a new type of tautomerism involving a shifting of an O instead of a H atom. The decompn. of other nitric esters, such as nitroglycerin, is analogous to that of A.

CHAS. A. ROUILLER

**Arsenical compounds related to arspenamine.** GEORGE W. RAIZISS AND JOSEPH L. GAVRON. *J. Am. Chem. Soc.* **43**, 582-5(1921).—Believing that the alarming symptoms sometimes observed on injection of arspenamine (A) might be due to chem. impurities, R. and G. have prepd. a number of compds. closely allied to A which might appear in the drug as impurities in the course of manuf. The 4,3- $\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_4\text{AsO}_2\text{H}_2$  from which A is prepd. by reduction sometimes contains the di- $\text{NO}_2$  deriv. and it is possible that A may sometimes be contaminated with 3,5,3',5'-tetraamino-4,4'-dihydroxyarsenobenzene tetrahydrochloride (B), which was prepd. by reduction of the di- $\text{NO}_2$  acid with  $\text{Na}_2\text{S}_2\text{O}_4$ ; it apparently exists in 2 forms, both yellow and easily sol. in cold  $\text{H}_2\text{O}$  but only one of which easily dissolves in MeOH. The prepn. and properties of the following additional compds. are described: 3,5-Diamino-, 3,5-diacetylamino-, 3-amino-, and 3-acetylamino-4-hydroxyphenylarsonic acids, 3,3'-diacetylamino-4,4'-dihydroxyarsenobenzene and the tetraacetyl derivative of B.

CHAS. A. ROUILLER

**Perchloromethylmercaptan.** O. B. HELFRICH AND E. EMMET REID. *J. Am. Chem. Soc.* **43**, 591-4(1921); cf. Frankland, Challenger and Webster, *C. A.* **14**, 3068. —The  $\text{CSCl}_4$  was obtained in 65% yield from a measured amt. of  $\text{CS}_2$  containing 0.3-0.4% I chlorinated in diffused light at 20-30° until the vol. is just doubled, allowed to stand 48 hrs., distd. up to 100° to remove most of the  $\text{SCl}_2$ , distd. with steam, dried and fractionated *in vacuo*. It is a yellow oil,  $b_{36}$  73°,  $b.$  149° (some decompn.), about  $1/8$  as toxic for dogs and  $1/8$  for mice as  $\text{COCl}_2$ . On reduction with Zn and HCl it disappears completely, apparently as  $\text{CH}_4$ ; Fe and HCl give a mixt. of  $\text{CCl}_4$  and  $\text{SCCl}_2$ ; refluxed with Fe filings it yields only  $\text{CCl}_4$ . Attempts to replace one of the Cl atoms by F failed; when the  $\text{SCCl}_4$  was refluxed with  $\text{ZnF}_2$  the product was nearly pure  $\text{CCl}_4$ .

CHAS. A. ROUILLER

**The role of mercuric nitrate in the "catalyzed" nitration of aromatic substances.** I. TENNEY L. DAVIS, D. E. WORRALL, N. L. DRAKE, R. W. HELMKAMP AND A. M. YOUNG. *J. Am. Chem. Soc.* **43**, 594-607(1921).—When  $\text{HNO}_3$  containing Hg in soln. acts on  $\text{C}_6\text{H}_6$  and some of its derivs.,  $\text{NO}_2$  groups are introduced but there is also some other reaction or series of reactions; one of the H atoms on the nucleus is replaced by a HO group, with formation of nitrophenols. Thus,  $\text{C}_6\text{H}_6$  warmed with com.  $\text{HNO}_3$  containing  $\text{Hg}(\text{NO}_3)_2$  gives  $\text{PhNO}_2$  and picric acid (A), the latter in such yields that this method can compete favorably with others for the prepn. of A from  $\text{C}_6\text{H}_6$ . The most plausible explanation is that the  $\text{C}_6\text{H}_6$  is first nitrated, that the  $\text{NO}_2$  group renders the o-H atom labile and active, that this H is oxidized to HO and that the resulting nitrophenol is nitrated to A. The authors find, however, that this hypothesis is untenable. Com.  $\text{HNO}_3$  containing enough  $\text{Hg}(\text{NO}_3)_2$  converts  $\text{C}_6\text{H}_6$  completely into  $\text{PhNO}_2$  and A while the same  $\text{HNO}_3$  without Hg salts leaves a large part of the  $\text{C}_6\text{H}_6$  unaffected. Dil.  $\text{HNO}_3$  (about 10%) boiled with  $\text{C}_6\text{H}_6$  in the presence of  $\text{Hg}(\text{NO}_3)_2$  gives considerable 2,4- $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{OH}$  but scarcely enough  $\text{PhNO}_2$  to be detected by its odor. Increasing concns. of  $\text{HNO}_3$ , even if  $\text{Hg}(\text{NO}_3)_2$  is present, give decreasing yields of A; with about 70% and stronger  $\text{HNO}_3$  the process is no longer practicable for the prepn. of A, while the yields of mono- and dinitrobenzene are good. A is oxidized and destroyed by boiling with strong  $\text{HNO}_3$ . The fact that expts. with strong acid in the presence of  $\text{Hg}(\text{NO}_3)_2$

gave good yields of nitrohydrocarbons shows that whatever A may have been formed (and conceivably oxidized) was less than the amt. which is produced with less concd. acid and that the production of A is, therefore, not due merely to the oxidizing action of the  $\text{HNO}_3$ . When  $\text{HNO}_3$  containing  $\text{Hg}(\text{NO}_3)_2$  was boiled 4 hrs. with  $\text{PhNO}_2$  under conditions which would produce A from  $\text{C}_6\text{H}_6$  itself, more than 0.5 of the  $\text{PhNO}_2$  was recovered unchanged, along with a small amt. of  $\text{C}_6\text{H}_5(\text{NO}_2)_2$  and there was no evidence that any A had been produced. Of pure  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$  treated in the same way, about 82% was recovered unchanged and  $(\text{CO}_2)_2\text{Hg}$  was isolated. *sym*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$  and 2,4,6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{Me}$  are practically unchanged. No A could be detected in any of the expts. The losses by destructive oxidation were least in the cases of those substances containing the most  $\text{NO}_2$  groups.  $\text{Hg}(\text{NO}_3)_2$ , therefore, does not favor the oxidation of the H atoms of a nitrated aromatic nucleus. In the prepn. of  $\text{C}_6\text{H}_4(\text{NO}_2)_2$  from  $\text{PhNO}_2$  the yield is smaller if an equiv. of  $\text{Hg}(\text{NO}_3)_2$  is added to the reaction mixt. The Hg, therefore, does not catalyze the introduction of  $\text{NO}_2$  groups. With  $\text{PhMe}$  and  $\text{PhCl}$  instead of  $\text{C}_6\text{H}_6$  were obtained trinitro-*m*-cresol and trinitro-*m*-chlorophenol, resp., from which the authors conclude that the HO and at least one of the  $\text{NO}_2$  groups are introduced simultaneously and that the course of the reaction probably involves the intermediate formation of a complex mol. compd. Increase in the amt. of Hg increases the yield of A, although not in direct ratio. The hypothesis that the Hg takes part in the reaction leading to the formation of A is supported by the appearance of the reacting mass; when  $\text{C}_6\text{H}_6$  is added to  $\text{Hg}(\text{NO}_3)_2$  in com.  $\text{HNO}_3$  the acid quickly becomes deep brown and then nearly black if kept cool; very little  $\text{NO}_2$  is given off by the cold mixt. but on warming red fumes come off abundantly and the dark color of the soln. disappears. By working at low temps. A and  $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{OH}$  can be prepd. with the production of practically no  $\text{PhNO}_2$ . A study of the gases shows that  $\text{NO}_2$  is evolved abundantly during the first hr. of heating but falls off rapidly in amt. and further heating results in the slow but regular evolution of NO formed by the destructive oxidation of the A. In one expt. with 20 g.  $\text{C}_6\text{H}_6$  was isolated 8 g. of a black substance, evidently a complex intermediate compd., containing Hg and yielding A when heated with  $\text{HNO}_3$ . The evidence indicates that  $\text{C}_6\text{H}_6$  reacts with  $\text{Hg}(\text{NO}_3)_2$  in  $\text{HNO}_3$  to form a highly colored complex compd. which, on warming, is attacked by the  $\text{HNO}_3$  with regeneration of the  $\text{Hg}(\text{NO}_3)_2$ , liberation of  $\text{NO}_2$  and production of 2,4- $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{OH}$  which on further heating is nitrated to A and this is in part oxidized to  $\text{CO}_2$ .  $\text{H}_2\text{SO}_4$  interferes with the reaction and reduces the yield of A to little or nothing, possibly because the complex compd. of  $\text{HgSO}_4$  with the aromatic substance differs from that with  $\text{Hg}(\text{NO}_3)_2$ , making the nucleus susceptible to easy oxidation.

CHAS. A. ROULLER

Mercuri-organic derivatives. II. Nitrobenzene mercury compounds; an indirect method of mercurizing organic compounds. MORRIS S. KHARASCH and LYMAN CHALKLEY, JR. *J. Am. Chem. Soc.* 43, 607-12(1921); cf. *C. A.* 15, 92.—In the last few years some theories have been advanced to explain orientation in the  $\text{C}_6\text{H}_5$  nucleus from an electronic point of view; of these the structural formulas for  $\text{C}_6\text{H}_5$  proposed by Fry (*C. A.* 9, 1327) and by Vorländer (*C. A.* 13, 2348) deserve the most consideration. Inasmuch as there are cases in which a group supposedly enters the  $\text{C}_6\text{H}_5$  nucleus as a positive group but on hydrolysis is removed as a negative group, it must be assumed that intramol. oxidation and reduction take place and since this is always supposed to be the case whenever a positive group enters in the *o*- or *p*-position to a positive group already present, a postulate which, according to F., is a very strong point, in favor of his theory, it appeared desirable to consider this reaction more in detail and K. and C. chose as the entering group the salt of an element known to be positive under all conditions, viz. Hg; should intramol. oxidation and reduction take place between the Hg and the C the Hg would be immediately pptd. as metallic Hg. As the first step in elucidating the

structure of  $C_6H_6$ , it had to be detd. whether a positive group would orient an entering Hg group to the *m*-position. Dimroth in mercurizing  $PhNO_2$  and heating  $(BzO)_2Hg$  had obtained *o*-derivs. whose structure was proved by conversion into the corresponding Br-derivs. by treatment with aq.  $KBr_3$  (*Ber.* 35, 2870(1902)). K. and C. now find that the three  $O_2NC_6H_4SO_3H$  in alc. heated with  $HgCl_2$  in 50% alc. (cf. Peters, *Ber.* 38, 2567(1905)) give the corresponding  $O_2NC_6H_4HgCl$  in 50% alc. and the *o*-compd. is identical with that obtained by D. from  $PhNO_2$ . In all three, treatment with HCl replaces the Hg by H, indicating that the Hg remains positive when attached to the C atom of the nucleus. According to F.'s formula for  $C_6H_6$ , therefore, it would be necessary, in the case of *o*- and *p*- $O_2NC_6H_4HgCl$ , for the  $NO_2$  group to change its polarity; i. e., upon hydrolysis with NaOH it should be removed as  $NaNO_2$ . However, not a trace of  $NaNO_2$  can be detected when the *o*-compd. is boiled with NaOH. Moreover, D. has shown that  $C_6H_6$  and  $(AcO)_2Hg$  at  $115^\circ$  give *p*- $C_6H_4(HgOAc)_2$ , and that both Hg atoms can be removed with HCl (*Ber.* 32, 760(1899)); also, picric acid can be mercurized (Hantzsch and Auld, *Ber.* 39, 1105(1906)). K. and C. believe that these facts constitute quite important limitations to F.'s electronic theory of  $C_6H_6$ . The limitations to V.'s conceptions of the orientation of aromatic compds. and a new theory as to *o*- and *p*-substitution will appear in a future paper by K. and Jacobsohn. *o*- $O_2NC_6H_4HgCl$  (3 g. from 2 g. *o*- $O_2NC_6H_4SO_3H$  in 20 cc. alc. boiled 45 min. with 6 g.  $HgCl_2$  in 20 cc. each of alc. and  $H_2O$ ), faintly yellow crystals from 95% alc., m.  $185^\circ$ , gives no HgS with  $(NH_4)_2S$  but gives the test for inorg. Hg after boiling with HCl or Cl water; with boiling HCl it forms  $PhNO_2$ , is unchanged by boiling several hrs. with twice the calcd. amt. of 5% NaOH, gives *o*- $O_2NC_6H_4Br$  with the calcd. amt. of Br in KBr. *m*-Nitrophenylmercuric chloride (5.7 g. from 8 g. *m*- $O_2NC_6H_4SO_3Na$  in 40 cc.  $H_2O$ , 21 g.  $HgCl_2$  in 100 cc. alc. and 2.3 cc. AcOH boiled 20 hrs.), crystals from alc., m.  $236-7^\circ$ , does not lose its Hg to HCl as easily as the *o*- and *p*-compds., gives *m*- $O_2NC_6H_4Br$  with  $KBr_3$ . *p*-Isomer (0.7 g. from 1 g. somewhat impure *p*- $O_2NC_6H_4SO_3H$  in 10 cc.  $H_2O$  and 3 g.  $HgCl_2$  in 10 cc. each of alc. and  $H_2O$  boiled 15 hrs.), crystals from alc., m.  $265-6^\circ$  (decompn.), gives *p*- $O_2NC_6H_4Br$  with  $KBr_3$ .

CHAS. A. ROULLER

Reactions of the formamides. VIII. Some thiazolidone derivatives. F. B. DAINES, ROY IRVIN AND C. G. HARREL. *J. Am. Chem. Soc.* 43, 613-8(1921); cf. C. A. 12, 904.—This is a continuation of the earlier preliminary expts. in which it was shown that the complex  $-CO.CH_2S-$  in 4-thiazolidones exhibits the general properties of an acid  $CH_2$  grouping, combining with the formamides and yielding derivs. in which the methylene H is replaced by the aminomethylene complex:  $=CH_2 + RN:CHNHR \rightarrow =C:CHNHR + RNH_2$ . The expts. here given also show in somewhat greater detail that all the 4-thiazolidones are characterized by the same reactivity of the methylene H towards  $BzH$  and the substituted formamides. *2-m-Tolylimino-3-m-tolyl-4-thiazolidone* (A), obtained in 60-80% yield from  $(m-MeC_6H_4NH)_2CS$  heated 1 hr. in alc. with  $ClCH_2CO_2Et$  and 1 mol.  $C_6H_5N$  or with  $ClCH_2CO_2H$  and 2 mols.  $C_6H_5N$ , seps. from alc. in yellow prisms, m.  $154-5^\circ$ . *p*-Tolyl isomer (B), flat pale yellow prisms from alc., m.  $127^\circ$  (Pozzi-Escot, *Compt. rend.* 139, 1032(1904), gives  $115^\circ$ ); *hydrochloride*, gummy ppt. from  $C_6H_6$ , becoming cryst. on standing, m.  $195-205^\circ$  (decompn.), hydrolyzed by hot  $N KOH$  to  $(p-MeC_6H_4NH)_2CO$ . *3-p-Tolyl-2,4-thiazolidone*, fine needles from  $H_2O$ , m.  $162^\circ$ , is readily obtained by hydrolyzing B with alc. HCl and is also the main product in the synthesis of B with  $ClCH_2CO_2H$  without  $C_6H_5N$ . *2-p-Bromophenylimino-3-p-bromophenyl-4-thiazolidone* (C), m.  $183^\circ$ , was prepd. from  $(p-BrC_6H_4NH)_2CS$ , long needles from alc., m.  $188^\circ$ , which was obtained in 57.5% yield by boiling  $BrC_6H_4NHCS_2NH_4$  with  $H_2O$ . *Chloro analog* (D) pale yellow crystals from alc., m.  $165^\circ$ . When a mixed thiourea,  $RNHCSNHR'$ , is heated with  $ClCH_2CO_2H$ , in all the cases thus far studied only one of the two possible isomers is formed; the conditions which

det. which of the two is formed are being investigated. *2-Phenylimino-3-p-bromophenyl-4-thiazolidone*, thick prisms from alc., m. 175-6°, hydrolyzed by HCl to PhNH<sub>2</sub>, and *3-p-bromophenylimino-2,4-thiazolidone*, needles from alc. or H<sub>2</sub>O, m. 130°, also formed by hydrolysis of C. *2-Phenylimino-3-m-bromophenyl-4-thiazolidone*, m. 171°. *3-p-Chloro analog*, thick prisms from alc., m. 184-5°, hydrolyzed to PhNH<sub>2</sub> and *3-p-chlorophenyl-2,4-thiazolidone*, needles from alc., m. 136-7° (Beckurts and Frerichs, C. A. 10, 888, give 145°), also formed by hydrolysis of D. *2-m-Nitrophenylimino-3-phenyl-4-thiazolidone* is obtained as a gummy noncryst. mass, which could not be purified sufficiently for analysis but yielded a benzal deriv. with BzH and was hydrolyzed to m-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> and 3-phenyl-2,4-thiazolidone. *2-m-Tolylimino-3-m-tolyl-5-benzal-4-thiazolidone*, obtained in 83% yield from A heated 5 hrs. at 150° with BzH, pale yellow microneedles from CHCl<sub>3</sub>-EtOH, m. 175-7°. *p-Tolyl isomer*, yellow needles from alc., m. 197°, hydrolyzed by boiling alc. KOH to (p-MeC<sub>6</sub>H<sub>4</sub>NH)<sub>2</sub>CO and *3-p-tolyl-5-benzal-2,4-thiazolidone*, short needles from alc., m. 210°; *5-m-nitrobenzal analog*, brownish yellow crystals from CHCl<sub>3</sub>, m. 230°. *2-p-Bromophenylimino-3-p-bromophenyl-5-benzal-4-thiazolidone*, light yellow crystals, m. 220°. *Chloro analog*, greenish yellow needles from alc., m. 213°. *2-Phenylimino-3-p-bromophenyl-5-benzal-4-thiazolidone*, light yellow plates, m. 197-9°. *3-m-Bromo isomer*, pale yellow needles, m. 200-1°. *2-m-Nitrophenylimino-3-phenyl-5-benzal-4-thiazolidone*, yellow crystals, m. 193°. The following condensation products with formamides were prepd. by heating the components in an oil bath; in general, the yields were 50-60%. *2-p-Tolylimino-3-p-tolyl-5-anilinomethylene-4-thiazolidone*, from a mol. mixt. of B and PhN:CHNHPh heated 3 hrs. at 140-60°, bright yellow needles from alc., m. 168°, converted by boiling alc. KOH into (p-MeC<sub>6</sub>H<sub>4</sub>NH)<sub>2</sub>CO. *5-β-Naphthylaminomethylene compound*, obtained after 1 hr. at 200-30°, yellow crystals, m. 215°. *3-m-Tolyl-5-anilinomethylene-2,4-thiazolidone*, needles from alc., m. 211°, is obtained, together with m-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, on boiling with alc. KOH the yellow product, m. 130-65°, which is formed by heating PhN:CHNHPh and A under various conditons. *2-p-Bromophenylimino-3-p-bromophenyl-5-β-naphthylaminomethylene-4-thiazolidone*, fine yellow needles from CHCl<sub>3</sub>-EtOH, m. 190°. *Chloro analog*, greenish yellow crystals from alc., m. 204°. *2-Phenylimino-3-p-chlorophenyl-5-anilinomethylene-4-thiazolidone*, yellow needles from alc., m. 180°. C. A. R.

Petrol-alcohol chemical discovery (ELLIS) 22. Production of acetic and lactic acids from corn cobs (FRED, PETERSON) 16. Prosthetic group of blood pigment (KOSTER) 11A. The function of chromophore (LIFSCHITZ) 3. Rapid pyrogenic decomposition of formic acid (MULLER, PEYTRAL) 2. Pyrogenic decomposition of benzene and benzaldehyde (PEYTRAL) 2. Pyrogenic decomposition of allyl alcohol (PEYTRAL) 2. Methylation of dipeptides (KOSSEL, EDLBACHER) 11A. Melanin and humus. The formula of p-benzoquinone; the thermal rearrangement in the quinone series (STOLTZENBERG, STOLTZENBERG-BERGJUS) 11A. Automatic separator in esterifications and other preparations (HULTMAN, et al.) 1. Effecting chemical reactions (Brit. pat. 155,776) 13.

POPE, F. G.: *Modern Research in Organic Chemistry*. London: Methuen & Co. 7s. 6d. For review see *Intern. Sugar J.* 23, 103(1921).

Acetaldehyde. STOCKHOLMS SUPERFOSFAT FABRIKS AKTIEBOLAG. Brit. 155,775, Dec. 22, 1920. In the catalytic manuf. of AcH by passing C<sub>2</sub>H<sub>4</sub> into an acid soln. of Hg salts, the reaction liquid is continually withdrawn from the reaction chamber, purified, enriched with fresh Hg salts by anodic oxidation in an external electrolyzer, and returned to the reaction chamber. The C<sub>2</sub>H<sub>2</sub> is introduced by a pipe into the reaction

chamber containing a hot soln. of  $\text{HgSO}_4$  in dil.  $\text{H}_2\text{SO}_4$ , and the acetaldehyde formed is removed through the pipe. During the process, the reaction liquid is continually circulated by means of a pump through an up-current separator, where the  $\text{Hg}$  sludge and aldehyde resin are deposited, then through a distn. vessel provided with a steam-jacket for the expulsion of any remaining  $\text{ACh}$ , and finally through an electrolyzer, in which by oxidation of a  $\text{Hg}$  anode the liquid is enriched with fresh  $\text{HgSO}_4$  before being returned to the reaction chamber. The  $\text{Hg}$  mud from the separator can be converted into metallic  $\text{Hg}$  in any suitable way and introduced into the electrolyzer. Any ferric salts added to the reaction vessel for the purpose of diminishing the formation of mud do not require renewal, since the ferrous salts produced in the reaction vessel are oxidized in the electrolyzer. The steam-jacketed vessel can be replaced by a column app. or by a vacuum distn. vessel; in the latter case, the liquid is raised to the reaction temp. by passage through the steam-jacketed conduit. A suitable app. is specified.

**Aminophenol derivatives.** E. KOLSHORN. Brit. 155,575, Nov. 24, 1920. Addition to 145,614 (C. A. 14, 3427). The process described in the principal patent is modified by the use of epichlorohydrin instead of  $\alpha$ -monochlorohydrin or glycide in the production of *N*-dihydroxypropyl-*p*-aminophenol or its alkyl ethers. The chloro compd. first obtained is saponified by alc. potash.

**Aminophenol derivatives.** E. KOLSHORN. Brit. 155,576, Nov. 24, 1920. Addition to 145,614 (C. A. 14, 3427). In the production of *N*-dihydroxypropyl-*p*-aminophenol, the process described in the principal patent is modified by substitution of  $\alpha$ - or  $\beta$ -dichlorohydrin for  $\alpha$ -monochlorohydrin or glycide. The chloro compd. first obtained is saponified by alc. potash.

**Dichloroethylene.** DR. A. WACKER GES. FÜR ELEKTROCHEM. INDUSTRIE. Brit. 156,080, Oct. 22, 1920. Symmetrical tetrachloroethane and  $\text{H}_2\text{O}$ , both in the form of vapor, are together brought into contact with a metal, particularly  $\text{Fe}$ ,  $\text{Zn}$ , or  $\text{Al}$ . A mixt. of 2 stereoisomeric dichloroethylenes is then obtained from the reaction product by fractional condensation and distn.

**Extraction of *o*-methoxycinnamic acid from lignin of *Torreya nucifera*.** I. ODAIRA, C. CHIBA and Z. MIWA. Japan 36,039, Mar. 25, 1920. Chips of *Torreya nucifera*,  $12\frac{1}{2}$  kg., are mixed with 2%  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$ , 10 l., and digested for 48–72 hrs., then pressed and filtered. *o*-Methoxycinnamic acid is pptd. from the filtrate by  $\text{HCl}$ . The acid is obtained also by extn. of the chips with  $\text{MeOH}$  or  $\text{Me}_2\text{CO}$ . After distn. of the solvent, the acid is extd. from the residue with aq.  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$  and pptd. by  $\text{HCl}$ .

**Extraction of *o*-methoxycinnamaldehyde from *kaya*.** I. ODAIRA, C. CHIBA and Z. MIWA. Japan 36,401, May 18, 1920. Enough *kaya* (*Torreya nucifera*, Sieb. et Zucc.) is subjected to steam distn. to obtain a distillate of about 50 kg. The distillate is mixed with 10 kg.  $\text{NaCl}$ , extd. with 2 kg.  $\text{Et}_2\text{O}$  or petroleum ether and dehydrated with Glauber's salt. After distn. of the solvent, the residue is distd. *in vacuo*; the part  $b_p$  160–175° is collected and recrystd. from the mixt. of  $\text{Et}_2\text{O}$  and petroleum ether. The yield is about 70 g. The aldehyde is obtained also from 1 kg. *kaya* by cold extn. with 3 kg.  $\text{Et}_2\text{O}$  or petroleum ether for 24 hrs.

**Apparatus for chlorination by ultraviolet light.** T. OKINAKA and S. SAKAI. Japan 35,994, March 18, 1920. The app. consists of a closed chamber provided with a window having a lens of uvioi or quartz glass and two tubes opening at the focus of the lens and another tube for exit of the product. Chlorination is conducted at the opening of the tubes under the influence of ultraviolet light sent through the lens.

## 11—BIOLOGICAL CHEMISTRY

HATTIE L. HEFT, EDGAR G. MILLER, JR. AND WILLIAM J. GIBBS  
A—GENERAL

FRANK P. UNDERHILL

Sweetening power of *p*-hydroxyphenylurea derivatives. F. BORDACKER AND R. ROSENBUSCH. *Ber. pharm. Ges.* 30, 251-8(1920).—In order to throw further light on the relation of taste to chem. constitution, new derivs. of *p*-HOC<sub>6</sub>H<sub>4</sub>NHCONH<sub>2</sub> (A) were prepd. (*β*-Hydroxy-*p*-phenetyl)urea, from A, HOC<sub>6</sub>H<sub>4</sub>Cl and EtONa, plates, m. 160°. (*β,α*-Dihydroxy-*p*-propoxyphenyl)urea, from A, EtONa and  $\alpha$ -chlorohydrin, spherical cryst. aggregates, m. 156-7°. *p*-Carbamidophenoxyacetamide, from A, EtONa and ClCH<sub>2</sub>CONH<sub>2</sub>, leaves, m. 264°. Of the above prepd. derivs. only the first named possesses a slightly sweetish, bitter after-taste, while the *p*-anisylurea of Riedel is only about one-fourteenth as sweet as dulcin. The investigation is being continued.

W. O. E.

Synthesis of cyanic acid by oxidation of organic substances. New methods of analysis of this compound. R. FOSSÉ. *Bull. soc. chim.* 29, 158-203(1921).—See C. A. 15, 1142.

E. H.

The activity of phytase as determined by the specific conductivity of phytin-phytase solutions. F. A. COLLATZ AND C. H. BAILEY. *J. Ind. Eng. Chem.* 13, 317-8(1921).—See C. A. 14, 3878.

E. H.

The influence of colloidal solutions of metals on lower organisms and the causes thereof. OLGA VON PLOTHO. *Biochem. Z.* 110, 1-32(1920).—The reactions of several types of bacteria, algae, fungi and higher plants as well as protozoa, amebae, paramecium sp., etc., were studied under the influence of colloidal Au solns., containing 0.003% of metal at temps. from 15 to 20° for periods of 1-4 days. The deposition of the metal within the organism had no particular harmful influence outside of retarding fructification of the fungi and elongation of the hyphae. The membrane is alone concerned, but no chem. combination with the Au took place, the metal remaining in the elementary condition.

F. S. HAMMETT

Influence of colloidal solutions of metals after transferring the mycelia from various nutrient solutions. OLGA VON PLOTHO. *Biochem. Z.* 110, 33-59(1920); cf. preceding abstract.—The small organisms fix the metallic particles of the metal hydrosols; this retards their growth. This fixation is dependent on the presence of org. colloids in the hydrosol and is brought about by the surface of the organism. It takes place during the life of the organism. It is not a chem. combination, but is a condensation process brought about by the elec. charges of the factors concerned. The surface charge is positive in acid, negative in alk. solns.; the charge of the metallic particles is negative; consequently fixation only occurs in acid solns. Fixation occurs in the absence of org. colloid, but the degree of deposition is dependent upon the amt. of org. colloid present up to the point where its concn. inhibits fixation completely. The retardation of growth is considerable in Ag and Cu colloidal solns. and is the greatest in those solns. in which the particles are the smallest.

F. S. HAMMETT

Enzyme formation. E. KÖHLER. *Biochem. Z.* 112, 236-54(1920); cf. C. A. 15, 1331.—For the formation of active zymase several conditions must be satisfied. The necessary precursors must be present in the protoplasm; there must be a stimulus in the plasma through which the formation of the inactive precursors of the zymase is brought about, and there must be a stimulus for the activation of these precursors (their transformation into potentially active zymase). The expts. that are reported indicate that the liberation of the activity of one of the two stimuli mentioned follows that of the other and that there are sugars which affect as accelerators one of the proc-

esses more than the other, and that different sugars act differently in this respect. This reaction is called the "antagonistic sugar effect."

F. S. HAMMETT

**Uricase in seeds.** ANTONIN NĚMEC. *Biochem. Z.* 112, 286-90(1920).—Five g. of finely ground soy-bean meal were put in an Erlenmeyer flask with 100 cc. of a 3% K urate soln. and allowed to stand under toluene at 35° for from 24 to 144 hrs. without the presence of air, also with air being drawn through the flask. The enzyme activity was detd. by the amt. of  $\text{NH}_3$  produced. The results were uniformly positive and quite considerably higher in the aerated samples. Adequate control tests were made, demonstrating that the soy bean is capable of splitting off  $\text{NH}_3$  from uric acid as well as from urea.

F. S. HAMMETT

**Studies on protein reactions. III. Cataphoresis experiments on microorganisms.** A. V. SZENT-GYÖRGYI. *Biochem. Z.* 113, 29-35(1921); cf. *C. A.* 15, 376.—Using the microscopic slide method of study previously described (*C. A.* 15, 376) S. investigated cataphoresis in several groups of microorganisms. Bacteria tend to wander to the anode and trypanosomes go now to the anode and now to the cathode. No morphological basis could be detected for these differences in reaction.

F. S. HAMMETT

**The adsorption capacity of various charcoals.** F. HÖRST. *Biochem. Z.* 113, 90-110(1921).—H. studied the adsorption capacity of Merck's vegetable and animal charcoals, norite, and 2 samples of charcoal from Frei-Weinheim for methylene blue, I, strychnine, neurine, tetanus toxin, diphtheria toxin and ricin according to Wiechowski's (*C. A.* 8, 3597) and Joachimoglu's (*C. A.* 11, 610) methods. The results showed that with chem. defined poisons the methods give sharp and valid measures of the relative adsorption capacities of various charcoals but that the use of the true toxins, such as tetanus, ricin, etc., yields unreliable results.

F. S. HAMMETT

**Photodynamic phenomena: Induced phototaxis in *Paramecium caudatum*.** II. P. MRYZNER. *Biochem. Z.* 113, 145-75(1921).—M. studied the phobo-phototactic effect of strong light and the spectrum on *Paramecium caudatum*. This organism as well as other infusoria can be made sensitive to light by the addition to their suspensions of fluorescent coloring materials such as erythrosin and eosin. Positive or negative phobo-phototactic activity could be induced, as long as the organism was not harmed by too strong photodynamic action, according to the strength of the stimulus, which was detd. by the light intensity, color degree and  $\text{O}_2$  concn. In favorable cases the light effect followed illumination within 0.1 sec. In the spectrum it was evident that the max. effect was expressed by the absorption max. of the coloring matter dissolved in or combined with the living plasma. The opinion is further expressed that the oxidase and catalase reactions play important roles in the causation of the phototactic reaction.

F. S. HAMMETT

**The oxidation of cystine and other amino acids by blood-charcoal.** OTTO WARBURG AND ERWIN NEGELEIN. *Biochem. Z.* 113, 257-84(1921).—This paper takes up in considerable detail the absorption of cystine by blood-charcoal, the oxidation of cystine, tyrosine, and leucine after absorption by charcoal, and the end-products of and the influence of temp. on the oxidation of cystine. Some 60% of cystine is absorbed by 1 g. of charcoal from 100 cc. of a 0.034% soln. of the amino acid with an accompanying oxidation after a time of considerable extent as measured by the  $\text{O}_2$ -consumption method.  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4$  and  $\text{CO}_2$  are products of the reaction. The oxidation of cysteine is similar to that of cystine in its general direction. Tyrosine and leucine are both oxidized in the presence of charcoal; they yield  $\text{CO}_2$  and  $\text{NH}_3$ .

F. S. HAMMETT

**The influence of neutral alkali salts on diastases.** AMANDUS HAHN AND KARL HARPUDDER. *Z. Biol.* 71, 286-301, 302-10(1920).—There were used for this study stock solns. of 0.1 g. malt diastase in 1 l.  $\text{H}_2\text{O}$ , 2 cc. of saliva, which had been dialyzed till salt-free, dissolved in 0.5 l.  $\text{H}_2\text{O}$  and 1.5 g. sol. starch dissolved in 100 cc. hot  $\text{H}_2\text{O}$ .



all of which were dild. to appropriate concns. when necessary. The amt. of reducing sugar formed under the influence of various neutral alkali salts with and without buffers was detd. It was found that the optimum for malt diastase is a  $p_H = 4.7$ , for salivary diastase  $p_H = 6.4 - 6.5$ . The combination of salts with the buffers either retarded or accelerated their influence according to the reaction and concn. of the salt buffer mixt. The nature of the buffer activity is detd. not only by the concn. but also by the type of ions of the compds. concerned. The authors studied the wandering of the enzymes in the electrical field in the presence of neutral alkali salts in solns. buffered with Na acetate in various concns. and came to the conclusion that the activity of both maltase and salivary diastase is, in the broad sense, independent of the elec. condition of the enzyme in soln. The isoelec. point of both enzymes is displaced\* to the acid side and tends to be shifted in the acid direction by Na salts to a greater degree than by K salts.

F. S. HAMMETT

Penetration of electrolytes into gels. II. The application of Fourier's linear diffusion law. G. S. ADAIR. Physiol. Lab., Cambridge. *Biochem. J.* 14, 762-79 (1920).—The indicator method of detg. diffusion, as developed by von Fürth and Bubanovic (*Biochem. Z.* 90, 269; 92, 139(1918)) is deficient in that their method of calcg. the diffusion const. (that is, the amt. of salt in equiv. which would flow across an area of 1 sq. cm., if the concn. at one point was 1 equiv. per l. greater than that at another point, 1 cm. distant in the line of flow) merely gives ratios and not abs. values. To overcome this drawback, A. has developed a theoretical formula free from arbitrary constns., and illustrates how this formula can be applied.

BENJAMIN HARROW

Action of a Bulgarian ferment on maltose and sucrose. GEN ITSU KITA. *Bull. soc. chim. biol.* 2, 140-2(1920).—This enzyme has no action on maltose or sucrose, as has previously been stated by Bertrand and Ducháček (*C. A.* 3, 1993, 2825).

J. C. S.

Enzyme formation with *Aspergillus niger*. H. VON EULER AND S. ASARNOJ. *Fermentforschung* 3, 318-29(1920).—The investigation proceeded along lines similar to those adopted by Euler and Svanberg (*C. A.* 14, 1130) in the case of saccharase in bottom yeast. As far as saccharase is concerned, it is found that the total enzyme action remains almost unchanged if the well ground fungus material is brought into contact with sucrose soln. either after being warmed to a temp. at which the saccharase is not damaged or after being dried with or without toluene. Wohlgemuth's method can only be applied with difficulty to the estn. of amylase by the direct action of the fungus material on starch soln.; the sugar which is formed is best estd. by Bertrand's reduction method. For the type investigated, and under certain conditions, the inverting capacity,  $I_f = k \times g \text{ sugar} / g \text{ dry substance}$ , is found to be  $0.32 \times 10^{-3}$ . A fungus which had been grown on starch soln. with the addition of peptone had a saccharase activity about 30% higher than that of a specimen grown under similar conditions but in the absence of peptone. Addition of peptone to the nutrient soln., which otherwise contains only inorg. N, also influences the formation of amylase. The data of other workers with regard to the improvement in the formation of amylase, due to addition of starch to the nutrient soln., could be quantitatively confirmed.

J. C. S.

Toxic actions in enzymic processes. I. Inactivation of saccharase by heavy metals. H. VON EULER AND OLOF SVANBERG. *Fermentforschung* 3, 330-93(1920); cf. *C. A.* 14, 2502.—The expts. were performed by observing the inversion of sucrose by the saccharase soln. used previously (cf. *C. A.* 14, 2502). It is found that the toxic power of the Ag ion towards saccharase is considerably greater than that of the mercuric ion. The enzyme is thereby inactivated, but not destroyed, since its power is completely restored by removal of the heavy metal or by converting it into an insol. form

(by  $\text{HgS}$ ). The graph showing the relationship between toxicity and concn. in the case of  $\text{HgCl}_2$  resembles the dissociation curve, whereas complete proportionality is found in the case of  $\text{AgNO}_3$ . The substrate (sucrose) exercises a considerable protective action towards metallic poisoning, which must be taken into account in calculating the necessary amount of poison per enzyme unit. With small amounts of  $\text{HgCl}_2$ , the coefficient of inversion falls rapidly with the time. The degree of poisoning also depends on the length of time during which the  $\text{HgCl}_2$  and saccharase are in contact previous to inversion; "self-regeneration" of the enzyme occurs gradually, the process appearing to be analogous to the "Danysz" effect in immunochemistry. The concentration of free silver ions becomes greatly diminished after addition of the enzyme solution to a dilute solution of  $\text{AgNO}_3$ , but metallic or colloidal silver is not formed, so that it would appear that union occurs with some components of the enzyme solution; it is found by electrometric measurement that each cc. of enzyme solution (containing 56 mg. of dry substance) requires from 28 to 55 mg. of silver. The toxic action of auric chloride towards saccharase is of the same order as that of  $\text{HgCl}_2$ , while copper sulfate is much less poisonous, and  $\text{CaSO}_4$ , titanium sulfate, and uranium nitrate are scarcely toxic. The previous data concerning the inhibition of enzyme actions by heavy metals are collected. II. The inactivation of saccharase (invertase) by organic substances. HANS VON EULER AND OLOF SVANBERG. *Ibid* 4, 29-63(1920).—The most inactivating substances for saccharase are aniline and *p*-toluidine. The inactivating action of aniline can be partly eliminated by the addition of benzaldehyde or acetone to the inactivated enzyme. It is supposed that the aniline is combined with the saccharase through an aldehyde group, and that the compound of saccharase and aniline has the structure of a Schiff's base. Other aldehyde reagents, namely, phenylhydrazine, hydroxylamine, semicarbazide, HCN, and  $\text{NaSO}_3$  also inactivate the action of the enzyme. Of the amine reagents, some showed an activating influence; others did not. III. The influence of copper sulfate on the autolysis of the yeast cell. OLOF SVANBERG AND H. VON EULER. *Ibid* 4, 90-6.—Copper sulfate does not appreciably inhibit the action of saccharase (invertase). On the addition, therefore, of copper sulfate to pressed yeast, autolysis was inhibited, but the saccharase from the treated auto-fermented yeast did not pass more freely into the juice than in the case of the untreated yeast.

J. C. S.

Studies in fermentation. V. Enzyme formation through the action of ions. W. BIGGERMANN. *Fermentforschung* 4, 1-28(1920); cf. C. A. 14, 1345.—I. Amylose, amylopectin, and amylocellulose. A clear amylose solution can be obtained by extracting wheat starch with water at  $80^\circ$ . The extract residue B. considers to be "amylopectin." An amylose solution could not be obtained at the ordinary temperature from potato starch. The extract residues from wheat and pea starch, on being digested with filtered saliva, left a residue, which did not give the I reaction and behaved like cellulose. Potato does not contain this substance. II. The influence of salts on the autolytic cleavage of pure amylose. From the results B. obtained by studying the action of various salts on sol. amylose, he concludes that the sol. amylose forms a complex with certain ions which acts as an autolytic enzyme. Amylopectin is resistant to the action of saliva in the presence of those salts, and can therefore be separated from it in this way. It also is evident that the autolytic enzyme formed is not identical with the saliva enzyme (ptyalin?).

J. C. S.

Action of lipase. EMIL ABERHALDEN AND ARTHUR WEIL. *Fermentforschung* 4, 76-89(1920).—The action of lipase from cattle pancreas on optically active synthetic fats was studied with the object of ascertaining whether there is a connection between the structure and configuration of the substrate and the action of the enzyme. It was found that the enzyme was not specific in this respect. From the velocity of the sapon.

of the various fats, it is concluded that, besides the lipase, which degrades triglycerides, there is no esterase present in the enzyme. The activity of the glycerol ext. of the pancreas is weakened by ultrafiltration, but can be reactivated by the addition of the residue retained by the filter.

J. C. S.

The separation of histidine from arginine. A. KOSSEL AND S. EDLBACHER. *Z. biol. Chem.* 110, 241-5(1920); cf. *C. A.* 1, 595.—The presence of arginine is not necessary in order to effect the pptn. of histidine.

J. C. S.

The methylation of dipeptides. A. KOSSEL AND S. EDLBACHER. *Z. physiol. Chem.* 107, 45-51(1919).—Glycylglycine hydrochloride was treated with  $\text{Me}_2\text{SO}_4$  in the presence of NaOH. After two hrs., the mixt. was acidified with HCl, evapd. to dryness under diminished pressure, and the residue then extd. with MeOH in order to sep. the Na Me sulfate; a colorless sirup was eventually obtained. The methylated product was pptd. as the picrate, from which it was afterwards liberated and crystd. from alc., m. p.  $141^\circ$ . The aurichloride,  $\text{C}_7\text{H}_{14}\text{O}_2\text{N}_2$ ,  $\text{HAuCl}_4$ , melted at  $155^\circ$ . The argenionitrate,  $\text{C}_7\text{H}_{14}\text{O}_2\text{N}_2$ ,  $\text{AgNO}_3$ , has m. p.  $180^\circ$ . The free base, on hydrolysis with  $\text{H}_2\text{SO}_4$ , yielded, among other products, glycine and betaine. The methylation of *dl*-alanylglycine was carried out in the same way as that of glycylglycine. The aurichloride,  $\text{C}_6\text{H}_{12}\text{O}_2\text{N}_2$ ,  $\text{HAuCl}_4$ , obtained has m. p.  $105^\circ$ . On hydrolysis with  $\text{H}_2\text{SO}_4$ , glycine and *dl*-trimethyl- $\alpha$ -propiobetaine, m. p.  $240^\circ$ , were obtained. In both instances, 3 Me groups were therefore introduced into the dipeptide.

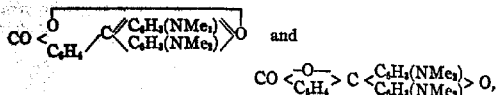
J. C. S.

The constitution of surinamine. E. WINTERSTEIN. *Z. physiol. Chem.* 107, 314-5 (1919); cf. *C. A.* 13, 3158.—W. points out the advantage of prep. surinamine from tyrosine by the method of E. Fischer and W. Lipschitz.

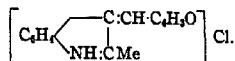
J. C. S.

Prosthetic group of blood pigment. Action of diazomethane on certain coloring matters and on anhydrous ferric chloride. WILLIAM KÜSTER. *Z. physiol. Chem.* 109, 108-16(1920); cf. *C. A.* 14, 3084.—According to the ordinary formula for hemin, the Cl is assumed to be united to Fe, although union with N is not excluded. In the action of diazomethane on different hemins showing marked differences as regards esterification, removal of the halogen has never been observed. K. [with O. Kusch] has now investigated the action of diazomethane on the hydrochlorides of various coloring matters of known constitution, and also on anhydrous  $\text{FeCl}_3$ . The results obtained indicate that true hemins are allied rather to this anhydrous chloride, which altered but little by diazomethane, than to the hydrochlorides of di- and tri-phenylmethane dyes, from which HCl is very easily withdrawn, with formation of  $\text{MeCl}$ . With the hydrochloride of a furylmethylindolenylmethane, the reaction is less ready, and with crystal-violet, reduction to the leuco base takes place. Finally, with a rhodamine hydrochloride no esterification occurs, so that the carboxyl group cannot be free, and an oxonium grouping must be assumed (cf. Noelting and Dzewowski, *Ber.*, 38, 3518-27 (1905)). The action of diazomethane on *Pyocyaninum coeruleum*, that is, on pentamethyl triaminotriphenylmethyl chloride,  $\text{NHMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CCl}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3$ , results in removal of 88.7% of the halogen. With *P. aureum*, that is, tetramethyldiaminodiphenylaminomethyl chloride,  $\text{NH}_2 \cdot \text{CCl}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , 79.2% of the Cl is withdrawn. Tetramethylrhodamine hydrochloride,  $\text{C}_{24}\text{H}_{20}\text{O}_2\text{N}_2\text{Cl}$ , obtained from dimethyl-*m*-aminophenol and phthalic anhydride, forms green plates with metallic luster, m. p. (dry)  $288-90^\circ$ , and dissolves in water or alc., giving a carmine-red soln. showing orange-yellow fluorescence. The free base is obtained in green leaflets exhibiting metallic luster, and dissolves sparingly in ether or light petroleum, and more readily in benzene

toluene, or xylene, giving colorless solns. The constitutions of the colored and colorless modifications of the base are



resp. In benzene soln. the anhydrous base is unaltered by diazomethane, which, however, withdraws 97.4% of the Cl from the hydrochloride, but does not esterify the base. The methyl ester of tetramethylrhodamine,  $\text{C}_{28}\text{H}_{30}\text{O}_4\text{N}_2$ , obtained by passing HCl into a soln. of the hydrochloride in MeOH, forms violet-red needles, m. p. 190°, is insol. in 5%  $\text{Na}_2\text{CO}_3$  soln. at the ordinary temp., but dissolves, with hydrolysis, in cold 1% NaOH soln., giving a red soln.; it is sol. also in HCl with a red coloration. *Furyl- $\alpha$ -methylindolylmethane hydrochloride*,



prepd. from furfuraldehyde and 2-methylindole, forms spherical aggregates, m. p. 300° (decompn.), the base being obtained as a brown ppt. on addition of NaOH soln. When suspended in acetone and treated with diazomethane, the hydrochloride loses nearly all its Cl. From an ethereal soln. of  $\text{FeCl}_3$ , diazomethane withdraws 6.71% of the Cl. J. C. S.

**Melanin and humus. I.** The formula of *p*-benzoquinone; the thermal rearrangement in the quinone series; the physiological significance of quinone humus. HUGO STOLTZENBERG and MARGARETE STOLTZENBERG-BERGUIS. *Z. physiol. Chem.* 111, 1-31 (1920).—*The decomposition of p-benzoquinone with boiling water.* *p*-Benzoquinone was heated in aq. soln. under a reflux condenser for 5 hrs. The residue was extd. with MeOH, and the substance thus obtained,  $\text{C}_{12}\text{H}_8\text{O}_4$ , was sol. in  $\text{NH}_4\text{OH}$  and alkali, from which it could be pptd. by acids. The calcium salt,  $\text{C}_{12}\text{H}_8\text{O}_4\text{Ca}$ , the magnesium salt,  $\text{C}_{12}\text{H}_8\text{O}_4\text{Mg}$ , the iron salt,  $\text{C}_{12}\text{H}_8\text{O}_4\text{Fe}'''$ , and the copper salt,  $\text{C}_{12}\text{H}_8\text{O}_4\text{Cu}$ , were obtained from it. On acetylating it with  $\text{Ac}_2\text{O}$  for 24 hrs., a compd. was obtained which showed that at least 3 of the O atoms were present in the form of hydroxyl groups. The residue from the decompn. mixt., which was insol. in MeOH, was dissolved in 0.1 N NaOH and reprecipitated with HCl; it had the empirical formula  $\text{C}_{24}\text{H}_{10}\text{O}_4$ . *Decomposition of p-benzoquinone by heat.* *p*-Benzoquinone was heated in a sealed tube at 165–85°, and the product extd. several times with boiling water and the residue treated with MeOH. A substance,  $\text{C}_{12}\text{H}_8\text{O}_4$ , similar to that obtained by the decompn. with hot water was identified. From this a *tetra-acetate*,  $\text{C}_{20}\text{H}_{16}\text{O}_8$ , was prepd. The residue, insol. in the MeOH, yielded a substance which contained more C than the analogous compd. from the hot-water decompn. A *tetra-acetate*,  $\text{C}_{20}\text{H}_{12}\text{O}_8$ , which agreed with the deriv. from a substance with the formula  $\text{C}_{12}\text{H}_4\text{O}_4$ , was prepd. On decompn. bromobenzoquinone by heat, a substance,  $\text{C}_8\text{H}_6\text{O}_2\text{Br}$ , was obtained, which was sol. in MeOH, and another one,  $\text{C}_{12}\text{H}_{4.46}\text{O}_{4.3}\text{Br}_{1.47}$ , which was not sol. in it. Similarly, substances with the formulas  $\text{C}_{12}\text{H}_7\text{O}_4\text{Br}$  and  $\text{C}_{12}\text{H}_7\text{O}_4\text{Br}_2$ , resp., were obtained from dibromobenzoquinone by heat. The substances  $\text{C}_{12}\text{H}_8\text{O}_4$  and  $\text{C}_{24}\text{H}_{10}\text{O}_4$  were reduced with HI and phosphonium iodide in a sealed tube at 200°. By fractional distn., the following fractions were obtained: From  $\text{C}_{12}\text{H}_8\text{O}_4$ : 100–54°,  $\text{C}_{12}\text{H}_{10}\text{O}_{4.4}$ ; 165–200°,  $\text{C}_{24}\text{H}_{18}$ ; residue,  $\text{C}_{24}\text{H}_{18}$ . From  $\text{C}_{24}\text{H}_{10}\text{O}_4$ : 127–40°,  $\text{C}_{24}\text{H}_{12}$ ; 150–207°,  $\text{C}_{24}\text{H}_{12}$ ; residue,  $\text{C}_{24}\text{H}_{10}\text{O}$ . On extg. with MeOH the black wax obtained by reducing  $\text{C}_{12}\text{H}_8\text{O}_4$ , a substance,  $\text{C}_{12}\text{H}_{10}\text{O}$ , was obtained. Similarly, a substance,  $\text{C}_{24}\text{O}_{10}$ , was yielded by extg. the black wax obtained as the reduction product of  $\text{C}_{24}\text{H}_{10}\text{O}_4$ . On oxidizing

$C_{15}H_{10}O_4$  with  $HNO_3$ , a product,  $C_{15}H_8O_6$ , was obtained. The bearing of the polymerization of the quinones on the physiology of the animal cell is discussed. J. C. S.

**The quantitative action of enzymes.** G. TAMMANN AND O. SVANBERG. *Z. physiol. Chem.* 111, 49-67 (1920).—The ideal action of an enzyme, which the action of emulsin on salicin resembles, is discussed mathematically. J. C. S.

**The methylation of proteins.** J. HERZIG. *Z. physiol. Chem.* 111, 223-7 (1920).—Some theoretical observations in connection with the methylation of proteins, in view of the results obtained by Edlbacher (*C. A.* 14, 1811) and by Herzig and Wandsteiner (*C. A.* 13, 328). J. C. S.

**Fate of  $\beta$ -naphthylamine in the organism of the dog.** ENGER. *Zentr. Gewerbehyg. Unfallverhüt.* 8, 816.— $\beta$ -Naphthylamine hydrochloride (1.0 and 0.5 g.) was administered to two dogs which were in a condition of N equil. and had a constant N and S elimination. Signs of illness were not observed. After the injection, the amts. of  $EtHSO_3$  and glycuronic acid in the urine were increased, and this lasted for 5 to 6 days. The ratio of the 2 acids indicated that much the greater part of the amine is eliminated in conjunction with the ethylsulfuric acid, at any rate in the case of carnivorous animals. In one expt. with a carbohydrate diet, only  $1/4$  of the amine was associated with ethylsulfuric acid, the remainder with glycuronic acid. The increment in the amts. of the two acids eliminated amounted in one expt. to 0.725 and 0.486 g. resp. Assuming that only aminonaphthols are formed, this would correspond with 1.444 g. of  $\beta$ -naphthylamine, which is more than was actually administered; it appears, therefore, that dihydroxynaphthylamines are also formed. Unchanged  $\beta$ -naphthylamine could not be detected in the urine. J. C. S.

**Action of sodium oleate on amylolytic fermentation.** TAMEKICHI ISAWA. The Kyoto Hospital, Kyoto. *Kyoto Igaku Zasshi (J. Med. Soc. Kyoto)*, 18, 49-82 (1921).—The action of unsatd. fatty acids on amylolytic and proteolytic fermentation was investigated, to find some connection between chem. action and immunity reactions. By the addition of a very small quantity of sodium oleate to a mixt. of amylolytic enzyme (such as pancreatin, Taka diastase, and serum diastase) and sol. starch, the action of the enzyme was inhibited distinctly, while peptic and tryptic fermentations are not influenced. Ovocithin has no influence on the diastase-starch reaction. The retarding action of the oleate is diminished by adding a soln. of Witte peptone or heated serum, which depends on the combination of protein or lipid with the oleate, but not on the protecting property for destroying enzyme. The oleate combines with blood corpuscles, serum-protein and peptone, but not with complement in serum by itself. When sodium oleate was previously added to amylase soln., amylolytic power was not altered, but when it was added first to starch soln., much more time was needed for complete digestion, compared with that of control expts. The oleate therefore neither destroys nor inactivates the enzyme, but probably makes a loose union with sol. starch, producing comparatively large granules and rendering the enzyme action on it very feeble. In the retarding influence of any substance on enzyme action, there are 4 possibilities at least, which should be distinguished: (1) simple inactivation; (2) destruction of enzyme; (3) combination of both inactivation and destruction; and (4) combination of the substance with substrate, making fermentation difficult or impossible. K. K.

**Nature of vitamins and their mode of action.** P. PORTIER. *Bull. soc. sci. hyg.* 8, 521-53, 603-20 (1920).—To this extensive review P. states the following conclusions: In addition to restoring the loss of bodily substance, and producing energy, foods have another role to play. They must furnish the anatomic element an impetus without which it cannot live. This "nutritive fecundation" is apparently performed by the vitamins which ordinarily impregnate the nuclear substance. Up to the

present, life has never been seen to create itself and in the higher animals it appears that life may perpetuate life only by life itself.

L. W. RIGGS

**Study of colostrum.** CH. PORCHER and L. PANISSET. *Compt. rend.* 172, 181-3 (1921).—The work was mainly histologic. It appears that colostrum is the remains of a phagocytosis of a milk previously produced. The lactose being a crystalloid is reabsorbed, and the action of the leucocytes upon the proteins changes a part of the latter into forms found in the colostrum.

L. W. RIGGS

**Utilization of vital wastes as agents of organic improvement.** LÉGRAND. *Rev. gén. sci.* 32, 37-44 (1921).—An address.

L. W. RIGGS

**Chemical phylogeny of the albuminoid molecule.** JOSÉ R. CARRACIDO. Univ. Madrid. *Rev. real acad.* 16, No. 4, Series 2; *Rev. sci.* 58, 711-20 (1920).—C. reviews the landmarks of org. synthesis relating to the chemistry of proteins from Wöhler to E. Fischer and Kossel. No new exptl. work is reported. Probable origins of chromatin and hemoglobin are suggested.

L. W. RIGGS

**Chemical basis of growth and longevity.** T. BRAILSFORD ROBERTSON. *Scientia* 29, 193-206 (1921).—A general discussion.

L. W. RIGGS

**Peroxidases.** II. RICHARD WILLSTÄTTER. *Ann.* 422, 47-73 (1921); cf. C. A. 13, 453.—The enzyme contents of plant materials are compared by means of the "peroxidase no." This is the no. of mg. of purpurogallin obtained when 5 g. of the plant material are worked up by the method previously described, and the product made up to a 200 cc. suspension, of which 5 cc. are taken for the detn. by the pyrogallol- $H_2O_2$  mixt. The peroxidase no.  $\times 40/5000$  gives the purpurogallin no. The peroxidase no. of horse-radish submitted to dialysis treatment, initially 880, falls to 801 after 4 days and then increases after 18 days to 1400. This variation is due, not to repression and stimulation of the enzymic activity but to formation of fresh peroxidase, so long as the plant cells retain their activity. When the dialysis is effected with  $H_2O$  containing  $C_7H_8$ , the formation of new peroxidase does not occur, and the peroxidase no. falls rapidly, owing to exosmosis of the enzyme. Similar phenomena have been observed in the case of other plant roots. The peroxidase no. of horse-radish attains its max. value after dialysis for about 3 wks., and from this it would appear that this duration of dialysis should result in the optimum yield of peroxidase ext. This, however, is not the case, all the evidence indicating that the plant material contains 2 peroxidases, one easily sol., the other quite insol. in  $H_2O$ . Horse-radish is dialyzed several wks., and at definite intervals portions are removed and thoroughly extd. with  $H_2O$ , the ext. and the insol. portion are sepd. in a centrifuge and the peroxidase no. of each is detd. The amt. of the sol. enzyme attains its max. value after 11 days dialysis; after 4 to 5 wks. it has fallen to less than  $\frac{2}{3}$  of its initial value, while the amt. of the insol. enzyme has increased to 2.5 its initial value. For the prepn. of the peroxidases, therefore, the plant material appears to be in the best state after dialysis for 6 to 12 days. The difference between the sol. and the insol. peroxidase is probably one of chem. constitution. As these substances are regarded as glucosides, it is possible that a component of the peroxidase mol. is combined with a simple sugar to form the sol. peroxidase, or with a more complex carbohydrate to form the insol. peroxidase. Based on the new experience gained, modifications of the method of W. and Stoll for extg. the crude peroxidase are described, the most important being the dialysis of the sliced roots for 7 to 9 days in water flowing at the rate of 100-150 l. per hr. A further step has been made in the purification of the peroxidase preps. by means of adsorption expts. with  $Al(OH)_3$  or  $Fe(OH)_3$ ,  $SiO_2$ , kaolin and talc. It has been found that a peroxidase prepn. (purpurogallin no. 573) in soln. in 50% alc. at a concn. of 0.05% is almost completely adsorbed by  $Al(OH)_3$  and that 90-95% of the peroxidase is recovered in soln. by agitating the adsorbate with  $H_2O$  containing

PhOH at 0-20°, the purpurogallin no. of the recovered peroxidase being 1000 to 1100. The adsorption method gives the best results with peroxidase preps. having high purpurogallin nos. A very great saving of time and trouble, however, can be effected and a prepn. of great activity obtained as follows: The dialysis of the plant material, the digestion with oxalic acid and with Ba(OH)<sub>2</sub> soln. and the removal of slimy substances by means of alc. are effected as already described, but the aq.-alc. filtrate (4-5 l.) instead of being evapd. to about 50 cc., is freed from CO<sub>2</sub> by a current of air and treated with quantities of 20-30 cc. of the adsorbent (3 g. Al(OH)<sub>3</sub> suspended in 100 cc. H<sub>2</sub>O) every 2-3 min. until 10-16 g. of Al(OH)<sub>3</sub> have been added. When the peroxidase reaction of a filtered portion is faint, a vol. of alc. equal to that of the Al(OH)<sub>3</sub> suspension introduced is added, the adsorbate is allowed to settle, the greater part of the soln. is decanted and the remainder centrifuged. The adsorbate is collected, treated with about 4 l. of twice-distd. H<sub>2</sub>O at 0°, and CO<sub>2</sub> passed in for about 0.25 hr. until the reaction is distinctly acid, and the soln. filtered, the clear filtrate evapd. *in vacuo* to 60-80 cc., again filtered, and treated with 5 vols. of abs. alc., whereby 0.31 g. of peroxidase prepn. (purpurogallin no. 860) is pptd.

C. J. Wess

**Astringency and protein-precipitation by masked tannin compounds.** TORALD SOLLMANN. Western Reserve Univ. *J. Pharmacol.* 17, 63-104(1921); cf. C. A. 15, 399.—The astringencies of "masked tannin compounds" have been compared with each other and with those of tannic acid under conditions simulating those occurring in the digestive tract. Various criteria of astringency were applied, including a new method employing blood corpuscles. All methods gave fairly concordant results. The simplest and therefore the most satisfactory appeared to be the pptn. of protein solns. This, in relation to the soly. and the taste of the drug, should give a fairly complete picture of its field of usefulness. Great variations in the compn. and the properties of different specimens of the commercial products rendered their classification difficult. However, the following conclusions appear justified: *Tannin-protein compounds.* Contrary to prevailing opinion, these dissolve rather better in artificial acid-gastric juice than in bicarbonate-trypsin solns. Their soly. is so slow, however, that they could be only slightly astringent in the stomach. Considerable astringency would develop in the duodenum, when the acidity is reduced. The effects would continue somewhat into the lower intestine following the cleavage of the undissolved proteinate. Slow soly. in bicarbonate soln. is therefore a desideratum if the action is intended to continue beyond the duodenum. *Tannin-acetyl esters.* Commercial brands are evidently mixtures of varying quality; some specimens apparently contain considerable free-tannin. The best specimens appear fairly uniform and but slightly sol. and astringent in acid soln. Bicarbonate dissolves them, and hydrolyzes them slowly. The astringency goes parallel to the hydrolysis, so that the action would continue for several hrs. and could thus extend into the lower intestines. However, they do not deserve full confidence until the commercial products are more uniform. *Other compounds.* The properties of those that were investigated do not appear promising (tannoform, tannopin, tannismuth, gallogen).

C. J. Wess

**Enzymes.** J. TAKAMINE and J. TAKAMINE. *Brit.* 152,792, July 24, 1919. Enzyme ext., prepd. by growing microscopic fungi, such as *Aspergillus*, *Penicillium*, *Mucor*, or *Eurotium oryzae*, on suitable culture media such as comminuted cereals, and then extg. with H<sub>2</sub>O and filtering, are sterilized by the joint action of heat and an antiseptic such as H<sub>2</sub>SO<sub>4</sub>. The process may be effected by adding the antiseptic to the enzyme ext. and passing the soln. through a copper coil at 45° into a sterilized container. The product has diastatic, proteolytic, milk-coagulating, and fat-splitting properties.

**The photoelectric theory of vision (POOLS) 3.**

## B—METHODS AND APPARATUS

STANLEY R. BENEDECT

**Preparation of Sørensen's phosphate solutions when the pure salts are not available.** C. J. MARTIN. *Biochem. J.* 14, 98(1920).—Recrystallize  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ . Dry in air between filter paper. Make a supposed  $M/7.5$  soln. of the recrystd. salt. Titrate 10 cc. of this against  $N/7.5$  NaOH, adding 0.05 cc. of 0.5% phenolphthalein as indicator. Add the soda until at  $18^\circ$  the color is of the same intensity as that of the 0.0035%  $\text{KMnO}_4$ . "For  $M/15$   $\text{NaH}_2\text{PO}_4$ , dissolve  $(138.1/15) \times (10/a)$  g. recrystd. salt and make up to 1 liter and for  $M/15$   $\text{Na}_2\text{HPO}_4$ , dissolve  $(131.1/15) \times (10/a)$  g. of the recrystd. salt in about 500 cc., add 66.66 cc. of  $N$  NaOH, and make up to 1 liter."  $a$  = cc. of NaOH required. To obtain any H-ion concn. between  $P_H = 6$  and  $P_H = 8$ , the 2 solns. are mixed in the proportions, as given by Sørensen (*C. A.* 5, 3835) and by Walpole (*C. A.* 5, 646; 9, 812). To prevent growth of molds, the solns. are shaken for a few min. with a little calomel and then filtered. B. HARROW

**Causes of error in tests for the detection of albumin and sugar in urine.** R. RINAUX. *J. pharm. Belg.* 3, 90(1921).—Tests with  $\text{HNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ , or acetic acid-ferrocyanide reagent, as well as the biuret reaction are not sufficiently sensitive to detect traces of albumoses in urine. In doubtful cases, where a ppt. is obtained with Esbach's reagent, but albumin cannot be identified, the tests should be repeated for several days on fresh samples before a conclusion is reached. A. G. DUMEX

**Physical methods for the examination of urine.** C. POSNER. *Ber. pharm. Ges.* 30, 465-74(1920).—An address. W. O. E.

**Progress and practice in the investigation of urine during the year 1919.** URZ. *Pharm. Monatshefte* 1, 33-40, 49-54(1920).—A review. W. O. E.

**Percentage and fractional dilutions.** B. BLACKLOCK. Liverpool. *Lancet* 1921, I, 377.—The following formula can be used where it is necessary to prepare specified vols. of lower % or higher diln. from higher % and lower dilns. respectively. Percentage diln.: To prepare a specified vol.  $z$  of a  $y$  % soln. from an  $x$  % soln., take of the latter  $xy/x$  vol. and make up to  $z$  vol. with dilg. fluid. Example: To obtain 12 cc. of a 24% soln. from an 80% soln., take of the latter  $(12 \times 24)/80 = 3.6$  cc. and make up to 12 cc. with dilg. fluid. Fractional diln.: To prep. a specified vol.  $z$  of a  $1/y$  diln. from a  $1/x$  diln., take of the latter  $x/y$  vol. and make up to  $z$  vol. with dilg. fluid. Example: To obtain 60 minims of a  $1/100$  diln. from a  $1/10$  diln. take of the latter  $(60 \times 10)/100 = 6$  minims, and make up to 60 minims with diln. fluid.

E. B. FINK

**A study of non-protein nitrogen of human blood. II. Chemical pathology of the urea fraction with a critical study of methods.** JOH FRIGL. Hamburg. *Z. exp. Med.* 12, 55-133(1921); cf. *C. A.* 14, 418.—Of the methods of urea N detn. the urease method of Folin and Wu was found to be exact. The values agree with those detd. by the rest N and non-urea N. Of equal value is the method of Fosse, modified by Mes-trezat. Next in importance is placed the sp. extraction method of Bang which is open to all the objections of the most exact microchem. methods of urea N detn. Values for urea N become less comparable the more complicated the methods of detn. The need is not so much for the development of new principles as for a simplification of existing methods. New methods for the detn. of peptide N, chromogens, amino acids and purines may be necessary and important. Such methods will be applicable to the study of liver pathology and the azotemia of Bright's disease. E. B. FINK

**Water-soluble vitamins and compounds which accelerate fermentation. I. Method of determination and preparation of the accelerating substances from yeast and rice sediment.** S. FRÄNKEL AND E. SCHWARZ. *Biochem. Z.* 112, 203-35(1920).—The method of detg. the accelerating effect on fermentation of various compds.



was to put 5 cc. of a 10% yeast suspension made from fresh pressed yeast-cake, in a gasometer and add 10 cc. of a 10% sucrose soln. An amt. of  $H_2O$  was added to the controls equiv. to the amt. of ext. added in the test. All tests were made in the thermostat at  $28^\circ$ , the  $CO_2$  production under these conditions during a period of 2 hrs. being taken as the measure of the relative activity of the yeast alone and yeast plus the stimulating substances. Extensive details are given of the methods used in the attempts at isolating the accelerating substance from the yeast and rice products. They can be summarized as follows: Incompletely dried yeast is mixed with 80% alc., the  $R_2O$ -sol. fat is removed and a preliminary pptn. with Pb acetate is made. The active filtrate is freed from Pb with  $H_2S$  and then pptd. with concd.  $HgCl_2$ . The ppt. is decompd. with  $H_2S$  freed from  $HCl$  with Pb and Ag, and allowed to stand in a vacuum, when inactive crystals are formed. The active sirup is pptd. with picrolonic acid, the inactive picrolonate is filtered off, and the filtrate, after the removal of the picrolonic acid with phosphotungstic acid, is pptd. with an excess. The ppt. which is active is treated with  $Ba(OH)_2$  and then  $H_2SO_4$  is added. The vacuum concd. filtrate contains the base as the sulfate and is 22 times as active as the first alc. ext. An attempt to shake out the active principle with amyl-alc. from the final sirup made alk. with  $NaHCO_3$  was unsuccessful.

F. S. HAMMETT

The microchemistry of chitosan compounds. H. BRUNSWIK. *Biochem. Z.* 113, 11-24(1921).—B. has collected together, tested out and enlarged upon the various macrochemical tests for chitosan and its salts. The crystn. of chitosan nitrate, sulfate and chromate is used to control the microchem. detection of chitin in plants. The chitin-containing substance is heated 15 min. at  $160^\circ$  with 50%  $KOH$ . The chitosan formed in this process is sepd. from the alkali by alc. and  $H_2O$  and tested on a glass slide with 50%  $HNO_3$ , 10%  $H_2SO_4$  or 1% chromic acid. When the mixt. is carefully warmed to the b. p. and then rather slowly cooled the respective chitosan salts crystallize out in characteristic spherule forms. The spherulites show polarization and are colored selectively with certain acid aniline dyes.

F. S. HAMMETT

Study of Bang's method for the microdetermination of glucose. S. A. HOLBØLL. *Biochem. Z.* 113, 200-9(1921); cf. Bang. *C. A.* 13, 2228.—H. repeats *in extenso* Bang's method for sugar detn. and concludes that the principles on which it is founded are exact and that there is a const. relation between the amt. of reduced  $KIO_3$  and the glucose content of the sample. He found, however, a  $KIO_3$  utilization of 0.265 cc. 0.1  $N$   $KIO_3$  for 0.1 mg. glucose instead of the 0.28 cc. value given by Bang.

F. S. HAMMETT

The determination of oxalic acid and oxaluric acid in urine and feces. A. BAU. *Biochem. Z.* 114, 221-57(1921).—A reagent for the detn. of oxalic acid in urine is prepd. as follows: (a) a mixt. of 330 g. of Na acetate and 300 cc.  $H_2O$  is warmed to soln., cooled and filtered if necessary. (b) 25 g. of crystd.  $CaCl_2$  is dissolved in 50%  $AcOH$ , put into a 500-cc. graduated flask and filled to the mark with (a). This soln. is allowed to stand at  $7^\circ$  for 48 hrs. and is then filtered through a hard S. & S. filter. For the analysis of urine, a measured amt. of the filtered specimen is taken,  $\frac{1}{6}$  its vol. of the reagent is added and the whole is allowed to stand for 38 to 44 hrs. in the cold. The ppt. is filtered, washed, ashed, heated to whiteness, weighed and titrated with 0.1  $N$   $HCl$ . The presence of glucose or albumin in the urine does not interfere with the accuracy of the detn. Oxaluric acid is not pptd. by the reagent. This latter compd. is detd. by 1st changing it to oxalic acid by boiling with  $HCl$  and following the procedure outlined above. The detn. of oxalic or oxaluric acid in feces is preceded by defatting, and drying, after which a satisfactory extn. can be made with  $HCl$ . This ext. is neutralized with  $NH_4OH$ , buffered with a neutral soln. of  $NH_4$  citrate and the detn. of oxalic acid is carried out as indicated.

F. S. HAMMETT

The normal presence of bromine in animal tissues. A. DAMIENS. *Bull. sci. pharmacol.* 28, 85-93(1921).—See C. A. 15, 219. F. S. HAMMETT

Diagnostic points of value found in the urine. W. H. PORTER. *Med. Rec.* 99, 465-70(1921).—A distinctively written essay on the use of the simpler methods of urine analysis in diagnosis. F. S. HAMMETT

A simple apparatus for gas analysis in physiological experiments. H. TRÜNDEL-BURG. *Z. Biol.* 72, 141-62(1920).—An extensive description of a rather simple app. and its use for detg. the gases in blood, etc. F. S. HAMMETT

A modification of the Barcroft and Winterstein micro-respirometers. N. K. ADAM. Biochem. Lab., Cambridge. *Biochem. J.* 14, 679-85(1920).—The app. is designed for taking observations on the rate of absorption of O by an isolated frog muscle in any desired atm.; simultaneous observations on the tension of contraction may also be made. (See also Winterstein, C. A. 7, 1028.) B. HARROW

The iodometric estimation of the sugars. J. L. BAKER AND H. F. E. HULTON. *Biochem. J.* 14, 754-56(1920).—Details regarding the use of the method of Willstätter and Schüdel (C. A. 13, 406), depending upon the oxidation of the sugar to the corresponding monobasic acid by means of I in alk. soln. BENJAMIN HARROW

The estimation of hematin in the whole blood. FRÉD VILÉS. *Bull. soc. chim. biol.* 2, 125-32(1920).—Two methods, depending on the transformation of a mixt. of oxyhemoglobin and hematin into one of reduced hemoglobin and reduced alk. hematin, or one of carboxyhemoglobin and reduced alk. hematin, resp., are described. The estn. is carried out by spectrophotometric means. J. C. S.

Detection of albumin in urine. WILHELM RADO. *Gyógyszerl.* 6, 66-7.—The test is applied by the addition of H<sub>2</sub>SO<sub>4</sub> (5%; about 1 cc.) and Na nitroprusside soln. (8 to 10 drops) to the filtered urine (5-10 cc.); in sensitiveness and clinical applicability, the test is equal to Boedecker's method with K<sub>4</sub>Fe(CN)<sub>6</sub> and AcOH. J. C. S.

Preparation of phosphomolybdic acid and its application to the colorimetric estimation of uric acid. P. PROSCHOWSKY. *Kongl. Vet. Landbohøjskole Aarskrift* 1918, 372-407.—P. reviews the colorimetric methods which have been proposed for the estn. of uric acid in urine, and indicates a new procedure for the prepn. of phosphomolybdic acid required in Höst's process; the latter has been examd. in detail, and certain improvements are recommended. J. C. S.

Microestimation of urea in blood by means of urease. R. BAHLMANN. *Ned. Tijdsch. Geneesk.* 64, [i], 473-8(1920).—The method of Cohen, Fervaert and Van Lier is modified in such a manner that the estn. can be made with 0.4 cc. of blood. The NH<sub>3</sub>, obtained by the action of the urease of the soy bean on the urea of the blood in faintly acid soln., is, after addition of alkali, drawn by a stream of air into very dil. HCl, and excess of the latter is estd. iodometrically according to Bang's method. A blank expt. is performed with an equal quantity of blood without addition of urease. The amt. of urea is calcd. from the difference in the titrations in the two expts. J. C. S.

Apparatus for the estimation of small quantities of urea. A. J. L. TERWYN. *Nederl. Tijdschr. Geneeskunde* 64, [ii], 875-80(1920).—The estn. of urea by Br and NaOH is liable to error, since NH<sub>4</sub> salts, creatine, uric acid, and hydroxyproteic acids can also yield N under these conditions, while also about 7% of the N is converted into other compds., and so escapes gas volumetric estn. For many clinical purposes, however, relative values are sufficient. An app. is described which permits in three flasks the rapid consecutive performance of two parallel expts., and a test with a known wt. of urea. A U-shaped capillary gas buret is attached which permits the gas to be measured under atm. pressure. J. C. S.

**Microestimation of dextrose by Bang's method.** BERTHOLD OPLER. *Z. physiol. Chem.* 109, 57-64(1920).—O. has tested this method (*C. A.* 13, 2228) with quantities of pure dextrose varying from 0.545 mg. to 0.027 mg., the ratio between the wt. of dextrose (mg.) and the number of cc. of 0.01 *N* iodate soln. increasing from 1:2.78 to 1:1.19, whereas Bang and Hatlehoel (*C. A.* 12, 2333) gave the const. value 1:2.8 for this ratio. No greater constancy of this ratio is achieved by the use of steam for boiling the soln. Hence, for the estn. of dextrose in the blood an empirical table is necessary. It is questionable if Bang's method really suffices for the estn. of sugar in a few drops of blood, and for the estn. of 1 mg. or less of dextrose Bertrand's method is recommended. J. C. S.

**Determination of micro-reduction.** D. G. COHEN TERVAERT. *Z. physiol. Chem.* 110, 41-54(1920).—The expts. here described show that Bang's modified method for the micro-estn. of sugar in blood (*C. A.* 12, 2333; 13, 2228; cf. also Maclean, *C. A.* 10, 1873; 13, 2889) is applicable only when the liquid is heated for a definite time. T. describes a simple method, consisting in oxidation by means of chromic acid, which allows of the estn. of dextrose, lactose, and maltose. As measured by this method, the reduction of the blood is higher than is indicated by the ordinary Cu methods. Dextrose added to blood is estd. quantitatively by this method. J. C. S.

**Nuclein metabolism. IX. Detection and estimation of combined and free purines in human blood and pus serum.** S. I. TEANNHAUSER AND G. CZONICZER. *Z. physiol. Chem.* 110, 307-20(1920); cf. *C. A.* 14, 1876.—For the estn. of the free purines in blood the serum is diluted with water and pptd. with 1.55% U acetate. The filtrate is boiled with some Na acetate and NaHSO<sub>3</sub> and pptd. with 10% Cu sulfate. The ppt. is centrifuged, washed, and the N in it is detd. by the micro-Kjeldahl method. From the value obtained, the free purine content is calcd. The figures of the uric acid content of serum obtained by the colorimetric method and by the above method agree fairly well, and it is therefore to be concluded that only very small quantities of free purines other than uric acid are present in the blood. In order to est. the combined purines (nucleotides) in the blood, the diluted serum is boiled, and pptd. with a 20% soln. of sulfosalicylic acid in order to remove the proteins. The filtrate is concd. and the purines are pptd. with Cu sulfate as previously described, and the total purines are obtained from the N estn., while the combined purines are calcd. by difference. 100 cc. of normal human serum contain 2-3 mg. of nucleotide N and 1-1.5 mg. of free purine N. J. C. S.

**Microestimation of dextrose by Bang's method.** ALBRECHT MERTZ. *Z. physiol. Chem.* 111, 43-8(1920).—By employing Bang's improved micro-method for the estn. of dextrose, a uniform reduction factor was obtained with quantities of 0.06-0.4 mg. of dextrose. The iodate soln. employed in the estn. is stable if pure reagents are employed. J. C. S.

**Maltose. II. Estimation of maltose in yeast.** RICHARD WILLSTÄTTER AND WERNER STEIBELT. *Z. physiol. Chem.* 111, 157-79(1920).—The fresh yeast is triturated with EtOAc until it liquefies, water is added, and the mixt. is neutralized with NH<sub>3</sub>. This yeast suspension is then made up to a definite vol. with a known maltose soln. and a buffer mixt.; aliquot portions are withdrawn at two different intervals, the degree of hydrolysis is estd., and the "time value" calcd. The few expts. carried out by this method show that most of the maltase of the yeast is extd. in this way. This method is also suitable for the comparison of the hydrolyses of sucrose and maltose by a given yeast. J. C. S.

**The estimation of very small quantities of arsenic in urine, blood, and other body fluids, and the arsenic balance in the silver salvarsan treatment.** HUGO ENCKELSON. *physiol. Chem.* 111, 201-22(1920).—The principle of the method is based on the

Ramberg-Sjöström method. The org. substance is decomposed by boiling with concd.  $\text{H}_2\text{SO}_4$  and fuming  $\text{HNO}_3$ , and the residual nitrogenous compds. are removed by heating with  $\text{NH}_4$  oxalate. After adding water,  $\text{HCl}$ ,  $\text{KBr}$ , and hydrazine sulfate, the As is distd. over as the trichloride, which is received in water and titrated with  $\text{KBrO}_3$ . By employing this method, it was found that the best part of the As of Ag salvarsan injected in a patient remained in the body after 16 days; only 26.6% of the total As was recovered in the urine.

J. C. S.

Refractive index determination and its importance in biochemistry. P. HIRSCH. *Z. angew. Chem.* 33, I, 269-71 (1920).—Various applications are discussed of the method for accurate detn. of the quantity of protein in very small amts. of substance. The importance is pointed out of measuring protein concn. of serum in normal and pathological conditions for which only a few drops of blood are required. Changes in blood vol. can also be studied with great accuracy by comparing the  $n$  of deproteinized serum before and after injecting some colloidal soln. This method is likewise applicable for detg. the protein content of therapeutic sera, for the study of progress of enzyme action, etc.

S. MORGULIS

New method of human calorimetry. III. The passage through the chamber of the current of air. Entrance, mixing and circulation. J. LEFÈVRE. *Bull. soc. hyg. aliment.* 8, 409-33 (1920); cf. *C. A.* 14, 759, 2654.—A critical discussion of the mechanism for admitting air to the calorimeter chamber. The following points are discussed from a theoretical standpoint: the best form of tube for admitting air to insure a desirable speed without sudden cooling of the subject, without pptn. of moisture on the inlets, and without sudden fall of pressure which might influence the calorimetric exactitude of the app. The pressure and velocity of the air are considered, the effectiveness of mixing with the air in the chamber, and the problem of uniform ventilation throughout the length of the distributing tube. I. discusses the thermodynamic phenomena which accompany the passage of the injected air, the work done, and the cooling produced by the expansion of this air. The paper is restricted to mathematical and theoretical deductions.

C. J. V. PRYTHONE

Gastric analysis. I. Fundamental principles. MARTIN E. REHFUSS AND PHILIP B. HAWK. *J. Am. Med. Assoc.* 76, 371-3 (1921).—A general discussion. Cf. *C. A.* 15, 1353.

L. W. RIGGS

Determination of small amounts of dextrose. Application to the cerebrospinal liquid. M. PIERRIER. *J. pharm. chim.* 22, 337-44 (1920); cf. *C. A.* 14, 2353, 3091, 3434.—The method of Bougault (*C. A.* 11, 2756) permits detn. of 0.165 g. of sugar per l.; the reaction is complete in less than 2 hrs. To det. sugar in the cerebro-spinal liquid (a), remove albumin with the reagent (b):  $\text{NaCl}$  15 g., glacial  $\text{AcOH}$  1 cc.,  $\text{H}_2\text{O}$  to make 100 cc. In a test-tube, mix 5 cc. of a with 2.5 cc. of b, heat for 3 min. in boiling  $\text{H}_2\text{O}$ , cool, neutralize with dil.  $\text{NaOH}$ , complete the vol. to 30 cc., filter. To 20 cc. add 1 cc. of a soln. of 15 g. crystd.  $\text{Na}_2\text{CO}_3$  per l., then 20 cc. of 0.01  $N$  I. After 2 hrs. contact, render acid with  $\text{HCl}$ , and titrate excess of I with a 0.005  $N$   $\text{Na}_2\text{S}_2\text{O}_3$  soln. For correction, subtract 0.1 cc. 0.01  $N$  I from the vol. consumed. 1 cc. of 0.01  $N$  I is equiv. to 0.9 mg. dextrose. Check detns. show the method to be exact.

S. WALDBOTT

Comparative results with Scales' method and Devarda's alloy for reducing nitric nitrogen (HARRISON) 7. Detection of volatile alkylamines in presence of ammonia and of volatile tertiary alkylamines in presence of volatile primary and secondary alkylamines (WOODWARD, ALABERG) 7. Apparatus for ultra-filtration (VILLEGAS) 1.

## C—BACTERIOLOGY

A. K. BALLS

The utilization of nitrates by molds for the production of nitrogenous compounds. S. KOSTYCHEV AND E. TSVETKOVA. *Z. physiol. Chem.* 111, 171-200(1920).—*Aspergillus niger* and *Mucor racemosus* reduce nitrates and nitrites to  $\text{NH}_3$ , from which they synthesize amino compds. with the help of sugar.  $\text{HNO}_3$ ,  $\text{NH}_3$ , and amino compds. have definitely been identified in the intermediate stages. The nitrite N is converted into  $\text{NH}_3$  and amino N outside the hyphae, but is not assimilated by them as such in expts. of short duration. The reduction of the nitrate to nitrite can be brought about without the addition of sugar, but the further utilization of the nitrite takes place, at least in *M. racemosus*, only in the presence of sugar. This reduction of nitrates has been demonstrated by a specially devised method. The old methods employed for such purposes are considered by the authors to be faulty. J. C. S.

The formation of sugar by molds from substances which are not sugars. S. KOSTYCHEV. *Z. physiol. Chem.* 111, 236-45(1920).—Sugar and alc. were formed by *Aspergillus niger* from the following substances: *d*-tartaric acid, glycerol, quinic acid, mannitol, and lactic acid. From peptone on the other hand, sugar was not formed. J. C. S.

A study of the variations in the hydrogen-ion concentration of broth media. LAURENCE F. FOSTER AND SAMUEL B. RANDALL. Univ. Calif. *J. Bact.* 6, 143-60 (1921).—Broth (beef infusion, beef ext., "bacto-beef"), adjusted to  $p_H$  values ranging from 5.0 to 9.0, undergoes a change in  $p_H$  upon autoclaving. The change is most marked in media adjusted to the alk. range (7.8-9.0), less in the acid range (5.0-6.2), and usually unappreciable in the neutral range (6.6-7.4). The max. change is about 0.4 and in most cases not over 0.2. The change is usually a decrease in  $p_H$  and not necessarily uniform in different expts. with media of the same compn. Autoclaved broth almost invariably decreases in  $p_H$  upon standing. Broth adjusted to  $p_H$  levels from 5.0 to 9.0 and exposed in tubes plugged with cotton to an atmosphere of  $\text{CO}_2$  for 24 hrs. increased markedly in acidity. The same changes occurred in an atmosphere of  $\text{CO}_2$ -free air as in ordinary air. Reaction changes in media of  $p_H$  5.2 to 9.2 do not appear to stand in relation to the changes in formol-titrating N. The possibility of an increase in acidity of broth through the opening up of  $-\text{COHN}-$  groups during hydrolysis of the protein constituents is pointed out. JOHN T. MYERS

The relation of hydrogen-ion concentration to the growth, viability, and fermentative activity of *Streptococcus hemolyticus*. LAURENCE F. FOSTER. Univ. Calif. *J. Bact.* 6, 161-209(1921).—*S. hemolyticus* is able to ferment the common hexoses and disaccharides but not the polysaccharides. The final  $p_H$  produced in broth containing various sugars varies between the limits 4.85-5.40. The lowest  $p_H$  is registered in broth containing glucose, the highest in broth containing lactose. The final  $p_H$  is usually attained in the second, not the first generation. Subsequent transplants do not show lower levels. Plain sugar-free broth cultures show a decrease in  $p_H$  probably due to a selective action on a portion of the protein mol. which acts like a carbohydrate. *S. hemolyticus* is able to produce its characteristic final  $p_H$  in neutral broth containing 0.2% glucose. Concns. of glucose up to 1% have no effect on the final  $p_H$ . The final  $p_H$  is not influenced by the presence of  $\text{K}_2\text{HPO}_4$  concns. up to 1% if sufficient glucose is present. Horse serum broth has a slight but distinct buffer effect. The curves of acid formation may be sepd. in 5 periods: stationary, lag, max., negative acceleration, and max. stationary period. The stationary and lag periods may be reduced to a minimum by an increase in the inoculum of the use of parent cultures of a suitable age. The presence of 5% horse serum in glucose broth reduces the lag in acid formation by 2 to 4 hrs. The most rapid formation of acid occurs in broth adjusted to a  $p_H$  of 8.1, while

a min. lag is shown at a  $p_H$  of 7.6. The optimum  $p_H$  for acid formation is believed to be 7.8. In plain broth the min.  $p_H$  permitting growth, the max. permitting growth, and the limits permitting luxuriant growth are, resp., 6.35, 8.50 and 6.60–8.50; in 1% glucose broth the figures would be, 6.35, 8.50 and 6.35–8.50; in 1% glucose, 5% serum broth they would be 5.70, 9.25 and 5.90–9.25. At a  $p_H$  of 5.25 lactic and acetic acids appear to have about equal disinfecting powers for *S. hemolyticus*. Organisms live longer in filtrates from active cultures than in broth brought to the same  $p_H$  with acetic or acetic acids. A marked increase in tolerance for acid is shown by streptococci in the presence of horse serum.

JOHN T. MYERS

**The biochemistry of *Streptococcus hemolyticus*.** LAURENCE F. FOSTER. Univ. Calif. *J. Bact.* 6, 211–37(1921).—Lactic acid appears to be the principal acid formed by *Streptococcus hemolyticus* in its fermentations of glucose broth. A smaller amt. of volatile acids is formed, made up chiefly of acetic with a trace of formic acid. A quant. study of  $NH_3$  excretion indicates that sugar in a medium has a "protein-sparing" effect by meeting the energy requirements of the developing cells. The max. periods of glucose utilization and acid formation in glucose and in glucose serum broth are correlated with a max. rate of growth, though a considerable lowering of  $p_H$  occurs during the period when the growth is diminishing. The greatest increase in  $NH_3$  output is correlated in a general way with max. periods of growth, glucose utilization, and acid formation. Associated with this increased output of  $NH_3$  is a decrease of amino acids. It is presumed that the amino acids are used for structural purposes. This would decrease the concn. in the medium and produce an increased excretion of  $NH_3$  through the katabolism of a part of the absorbed amino acids. A rise in the curve of amino-acid formation occurs after the organisms have made their growth, which is accompanied by a decrease in  $NH_3$  formation. This indicates that a decreased utilization of nitrogenous materials ensues after the organism has passed its max. period of growth, despite the fact that proteolysis continues. There is a marked difference in N metabolism between a lab. and a passage strain during the first three hours of incubation in glucose serum broth. The passage strain shows a decrease in amino-acid output coupled with an increased  $NH_3$  excretion, but the lab. strain shows a decided increase in amino-acid with a slight decrease in  $NH_3$  formation. It is not known whether this represents a permanent deviation in metabolism caused by repeated transplantation on artificial media or not. A long bibliography is appended.

JOHN T. MYERS

**Rose bengal as a general bacterial stain.** H. J. CONN. N. Y. Agr. Expt. Sta. *J. Bact.* 6, 253–4(1921).—Rose bengal has a great affinity for bacterial protoplasm but not for the slime and debris which surround the organism. It is of especial value for slime formers such as *B. radicumicola*. It is made up as follows: rose bengal, 1 g.; 5% phenol, 100 cc. The stain keeps several months.

JOHN T. MYERS.

**The production of volatile fatty acids by bacteria of the dysentery group.** HARPER F. ZOLLER AND W. MANSFIELD CLARK. Bur. Animal Ind. *J. Gen. Physiol.* 3, 325–30 (1921).—All of the organisms studied showed a close agreement in the total quantity of volatile fatty acids produced and in the ratio of formic to acetic acid, both under aerobic conditions and in the presence of 1% of glucose. Growth upon peptone alone with free access to the air resulted in the production of appreciable quantities of volatile fatty acids, but the solns. became more alk.; propionic acid was found but not formic. Exhaustion of air from the non-sugar media again brought about the formation of formic acid and in addition some butyric acid, in both Shiga and non-Shiga cultures, and the reaction of the media was distinctly more acid. When glucose was present in media from which the air had been exhausted, the type and degree of fermentation were about the same as those in similar media bathed in air at normal pressure. "The enormous quantity of formic acid produced by these bacteria may play a significant part in the

digestive disturbances and toxic symptoms accompanying their infection of the human intestinal tract." It is suggested that the large yield of formic acid from glucose by these bacteria may be of some commercial value. CHAS. H. RICHARDSON

**Poisoning by fungi of the genus *Inocybe*.** C. FAHRIG. *Arch. exp. Path. Pharm.* 88, 227-45(1920).—Following the observation of several cases of poisoning due to the ingestion of fungi, botanically characterized as *Inocybe frumentaceae* and *Inocybe sambucina*, a chem. and pharmacol. study was made of the fungi. The active toxic substance was found to be muscarine, 0.36 g. of which could be derived from 100 g. of the fresh fungi. G. H. SMITH

**Bacteria and blood pigments.** H. KAMMERER. *Arch. exp. Path. Pharm.* 88, 247-87(1920).—Of a large series of organisms studied only two, *Streptococcus hemolyticus* and the pneumococcus, oxidized hemoglobin to methemoglobin. The hemolytic activity of bacteria in fluid media and in solid media (blood agar plates) is associated with two entirely distinct processes. Clearing in the plate is due to tryptic activity and is produced by all bacteria which elaborate a tryptic enzyme. Hemolysis in fluid media is apparently due to rupture of the lipoid membrane of the red cell, through lipase action. Certain of the derivs. of the blood pigment exert a marked inhibitive and destructive action on bacteria, but this process is directed only against the Gram-positive organisms. The sensitizing action of light plays no part in the bactericidal action of mesohematin. Mesohematin prevents phagocytosis both *in vitro* and *in vivo*. Hematoporphyrin, bilirubin, etc., show none of these activities. G. H. SMITH

**Yeast crops and the factors which determine them.** A. SLATOR. *J. Chem. Soc.* 119, 115-31(1921).—As a result of these investigations it is suggested that some of our views of the factors which influence yeast growth must be considerably modified.  $\text{CO}_2$  is said to have a greater influence than that ordinarily believed and great variations in the crop are obtained by altering the concn. of  $\text{CO}_2$ . Air (O) has much less influence than is usually attributed to it. It plays no part in the initial budding of the yeast and has no direct accelerating effect during the 1st stages of growth. Later stages seem to be favorably affected; the aerobic vegetative growth comes into consideration here. Air decreases the supersatn. of the wort with  $\text{CO}_2$  and favors the growth. It is not as necessary for the development of the yeast as is usually believed. F. W. TANNER

The chemical potential of phenol in solutions containing salts, and the toxicity of these solutions towards anthrax and staphylococcus (LAIRD) 2. Preparation of some alkyl derivatives of resorcinol and the relation of their structure to antiseptic properties (JOHNSON, LANE) 10.

#### D—BOTANY

CARL L. ALSBERG

**Evaluation of climatic temperature efficiency for the ripening processes in sweet corn.** C. O. APPLEMAN AND S. V. EATON. Maryland Agr. Expt. Sta., *J. Agr. Res.* 20, 795-805(1921).—Stowell's evergreen corn from home seed was used in this study and early and late crops were grown. Starch, cane sugar, reducing sugars, fat, crude fiber and N were detd. Temp. indices in relation to ripening are given, also a comparison of predicted rates of ripening for sweet corn in different localities based upon exponential indices corresponding to the normal mean temps. of the ripening seasons. The localities selected were Charleston, S. C., Baltimore, Md., New Haven, Conn., and Portland, Me. The rate of ripening for sweet corn during August is calcd. from Baltimore temps. The rate of ripening within a wide range of temp. appears to adhere rather strictly to the van't Hoff-Arrhenius principle. Sweet corn is considered ripe when the growth of the kernels ceases and the chem. changes have nearly reached equilibrium. The maturing of corn consists chiefly in loss of  $\text{H}_2\text{O}$ . During ripening the

sugars decrease and the starch increases. In the very early stages of ripening the reducing sugars predominate; therefore the stage of highest total sugar content does not necessarily coincide with the stage of greatest sweetness. The % changes in fat, crude fiber and total N occur largely during the early stages of ripening. The rate of starch synthesis in the kernels seems to be the controlling factor for several supplementary processes. The rate at which the ratio of total sugar to starch decreases is a good measure of the ripening rate and was so used. Temp. is the controlling factor for the rate of ripening. The late crop of corn required 15 days for the same period of ripening for which the early crop required 6 days.

F. C. COOK

Comparative utilization of the mineral constituents in the cotyledons of bean seedlings grown in soil and in distilled water. G. D. BUCKNER. Kentucky Agr. Expt. Sta. *J. Agr. Research* 20, 875-80(1921).—The degree of utilization of the total ash and the elements Ca, Mg and P in the cotyledons of Kentucky Wonder bean seedlings grown in distd. H<sub>2</sub>O and in garden soil were compared. Analyses of whole beans and of cotyledons, embryos and integuments were made. When the beans were grown in soil a considerably larger amt. of reserve material was translocated from the cotyledons than when they were grown in distd. H<sub>2</sub>O. In both cases a smaller proportion of Ca was translocated than of P or Mg. The expts. are being continued.

F. C. COOK

Cellular absorption. A. TRÖNDLE. *Biochem. Z.* 112, 259-85(1920).—This lengthy report takes up the influence of narcotics and acids on salt absorption. The permeability of plasma for individual alkaloids is treated from the point of view of the absorption of the alkaloid bases and the alkaloid salts with a comparison between the free alkaloids and their salts. It is a report written by P. Stark after the death of the investigator and from his notes. The expts. were carried out on the palisade cells of *Buxus sempervirens* and *Acer platanoides*. When these cells are previously narcotized with Et<sub>2</sub>O or chloral hydrate, absorption of NaCl or KCl is completely suppressed, recovery from which occurs. Acids tend to increase the permeability, which is apparently a physical chem. phenomenon. The studies on the alkaloids were made with 2 spirogyrae, the moment of pptn. of tannin in the vacuole being used as the measure of the effect. Expts. with quinine, caffeine and piperidine showed that the product, time of pptn. and concn., is a const.

F. S. HAMMETT

The phytochemical reduction of acetol to optically active propylene glycol. E. FÄRBER and F. F. NORD. *Biochem. Z.* 112, 313-23(1920).—Phytochemical reduction in the presence of top-yeast of acetol to optically active propylene glycol occurs. This reaction shows that asymmetric reactions are a common biological property of both plants and animals.

F. S. HAMMETT

The role of the plant glucosides. R. WASICKY. *Biochem. Z.* 113, 1-18(1921).—The toxicity of the isolated living leaf of the red digitalis depends in great degree on whether or not the leaf has been kept in the sunlight or in the dark previous to the test. The toxic dose per g. frog ranges from 0.00025 to 0.0003 g. dried leaf substance after exposure to sunlight, and is about 0.0005 to 0.0007 g. after several hrs. in the dark. No differences in the relative results are obtained when the 1st-year ground leaves are compared with the stem-leaves of the 2nd year. Reducing substances are always to be found in the juice when the study has been prolonged for some time. Further studies were not uniformly successful in demonstrating the presence of an enzyme concerned in the glucoside soln. The toxicity of the ext. is undiminished by heating while in certain cases this decreased when the sample was allowed to stand, thus tending to show that enzymes are present. The mesophyll of the leaf is some 5 times as toxic as is the epidermis. In *Digitalis purpurea* the toxic glucosides undergo their formation and destruction in the cell sap.

F. S. HAMMETT



The superfluity of manganese for the oxidase molecule in the cultivation of *Hedera helix*, and Bertrand's manganese theory of the oxidases. A. W. VAN DER HAAR. *Biochem. Z.* 113, 19-28(1921).—H. discusses Bertrand's (cf. *Compt. rend.* 124, 1032) theory of oxidase activity, which implies the presence of a complex containing a Mn cation and an organic (protein) anion, and presents expts. which he thinks fail to substantiate the earlier idea. He was able to cause "Efeu" seeds to germinate without Mn, and to grow to normal development in H<sub>2</sub>O culture plus Mn-free salts. The presence of oxidase in these plants also was established. However, since he found 0.05 mg. of Mn in the ash of one of his plants, it would appear that the question is still unsettled. F. S. HAMMETT

The mobilization of the ash constituents and the nitrogen in twigs during the spring budding. AUGUST RIPPET. *Biochem. Z.* 113, 125-44(1921).—Detns. were made of the Ca, Mg, Na, K, P, N, Cl, and S of plants during the spring budding season. K, P, Mg, Na and N are mobilized from the ash, while Ca, Cl and S are but little, if any, changed. In the budding twigs there early occurs a lack of N and the mineral constituents at the time when carbohydrates are still present in quantity. All the mobilizable elements are almost entirely originally present in org. combinations and the lack of any one of them in the presence of all the others causes an increased mobilization of the deficient elements from the ash. The inability to resorb Ca causes the growing twigs to react more intensively to a lack of this element. F. S. HAMMETT

Chemical components of green plants. II. Presence of a mixture of unsaturated alcohols in many green plants. HARTWIG FRANZEN AND ADOLF WAGNER. *Sitzb. Heidelberg Akad. Wiss. Math. Nat. Klasse, Abt.* 1920, 2 reprints, pp. 4.—The mixt. of unsatd. alcs. found previously in the leaves of beech and chestnut is shown by its characteristic odor to be present also in the leaves of all classes of plants investigated (40 have been examd.). The distillate from the mountain ash also contained HCN, while a component with an intense odor of lemons (citral) was present in that from strawberry leaves. The first distillate from certain plants (wormwood, dahlia, peppermint, ivy) contained notable amts. of essential oils. J. C. S.

Carbohydrates of *Lichen islandicus*. E. SALKOWSKI. *Z. physiol. Chem.* 110, 158-66(1920); cf. *C. A.* 13, 2905.—S. confirms the statement of Errera (*Diss.*, 1882) and others to the effect that *Lichen islandicus* contains two carbohydrates: (1) lichenin, which gelatinizes when the hot soln. is cooled and gives no reaction with I, and (2) a sol. carbohydrate which, contrary to the statement of Ulander and Tollens (*Ber.* 39, 401(1906)) gives a decided blue coloration when carefully treated with I soln.; this coloration is, however, distinctly less intense than that obtained with starch, and it is possible that this carbohydrate, known as isolichenin, is not a single individual, and that the I reaction depends on the presence of a third carbohydrate in small proportion. The physical constitution of lichenin in the moist state suggests that this compd. either belongs to the pectins or contains these. Dry lichenin does not, however, respond to the method of detecting pectin given by von Fellenberg (*C. A.* 10, 2772), according to whom the pectins yield MeOH when treated with NaOH soln. J. C. S.

The character of the potassium compounds in living plant tissue. S. KOSTYCHEV AND P. ELLASBERG. *Z. physiol. Chem.* 111, 228-35(1920).—The total K of the plants examd. could be extd. with water. On incinerating the extd. residue, the ash was found to be free from K. The Pb acetate and tannin ppts. were also found to contain no K. The aq. exts. before and after incineration contained the same quantities of the element as estd. by Hamburger's method. K, therefore, unlike other indispensable elements, is not present in the plant, even partly, in combination with org. matter. J. C. S.

**Auxographic measurement of swelling of biocolloids and of plants.** D. T. MACDOUGAL. *Bot. Gaz.* 70, 126-36(1920); cf. *C. A.* 14, 2942.—The methods used in preparing some of the colloid mixtures are described. The auxograph is illustrated, and the results obtained with certain colloid mixtures are tabulated. T. G. PHILLIPS

**Swelling of agar in solutions of amino acids and related compounds.** D. T. MACDOUGAL AND H. A. SPÖHR. *Bot. Gaz.* 70, 268-78(1920); cf. preceding abstr.—The swelling of agar in water is surpassed only when dil. solns. of amino acids, or  $\text{NH}_3$  and its compds., are used. The possible biological significance of these expts. is emphasized.

BENJAMIN HARROW

**Presence of quinic acid in leaves of certain Coniferae.** GEORGES TANRET. *Compt. rend.*, 172, 234-6(1921).—Leaves of *Cedrus Libani* were twice extd. with 5 times their wt. of boiling 70% alc., the ext. pptd. with basic Pb acetate, the Pb removed by  $\text{H}_2\text{SO}_4$  and the AcOH washed out with ether. The resulting acid liquid is neutralized by  $\text{Ba}(\text{OH})_2$ , evapd. to a sirup and the sugars are removed by extrn. with boiling alc. The residue consisting of the Ba salt of the acid is dissolved in  $\text{H}_2\text{O}$ , basic Pb acetate added, Pb removed by  $\text{H}_2\text{S}$ , the soln. evapd., the residue treated with 90% alc., and the alc. evapd., giving anhydrous crystals very sol. in  $\text{H}_2\text{O}$ , sparingly sol. in 95% alc., m. 183-4°. The crystals heated with  $\text{H}_2\text{SO}_4 + \text{MnO}_2$  give quinone. The aq. soln. gives  $[\alpha]_D = -43.2^\circ$ . Leaves gathered near Paris in July yielded 5 g. of cryst. acid per kg., in Dec. 2 g. per kg. Preliminary expts. failed to isolate quinic acid from Taxaceae or Cupressineae. In Abietineae, the acid was not found in spruce or fir, but *Larix europaea* yielded nearly as much as *Cedrus*. Also in *Bull. soc. chim.* 29, 223-9(1921).

L. W. RIGGS

**Influence of the calcium-magnesium relation upon the growth of plants.** OSCAR LOWE. *J. Landw.* 68, 225-33(1920).—No general conclusions can be drawn from the literature which is cited.

F. M. SCHERTZ

**The action of sodium, accessory to potash, as a nutritive substance of plants.** TH. PFEIFFER, A. RIPPHEL AND CHARLOTTE PFOTENHAUER. *J. Landw.* 68, 256-284(1920).—By oats plants Na was found to be used as a substitute to some extent for K. Leaves and stems utilize Na, which also increases grain production. A general discussion and review of the literature are given.

F. M. SCHERTZ

Action of chloropicrin on higher plants (BERTRAND) 15.

## E—NUTRITION

PHILIP B. HAWK

### NORMAL

**Green feed versus antiseptics as a preventive of intestinal disorders of growing chicks.** A. G. PHILLIPS, R. H. CARR AND D. C. KENNARD. *Purdue Univ. J. Agr. Research* 20, 869-73(1921).—160 White Leghorn day-old chicks were used. Wt. and mortality data, the av. protein consumption and the amt. and distribution of feces N are given. N sol. in 0.1 N HCl is calcd. as urea, ammonia and amino acid N. The N insol. in 0.1 N HCl is called uric acid and residual N. Straw, green plus greens, HCl, tobacco, sulfur, lactose and  $\text{CuSO}_4$  were all added to the basal diet, which consisted of 50 parts cracked corn, 35 parts corn meal, 15 parts corn bran, 3 parts ash, 8.86 parts meat scrap and 10.9 parts soy-bean meal. Tops of sprouted oats seemed to be valueless as a preventive of digestive disorders or as an aid to the growth of chicks in confinement. Less uric acid was found in the feces from the chicks given HCl and tobacco powder than in the other cases. Tobacco powder prevents the normal growth of chicks and causes them to be wild and nervous. HCl, S, and particularly  $\text{CuSO}_4$  offer interesting possibilities of success in raising chicks in confinement. F. C. COOK

**The effect of alkali on the efficiency of the water-soluble vitamin.** B. THOMAS, B. OSBORNE AND CHARLES S. LEAVENWORTH. *Conn. Agric. Expt. Sta. J. Biol.*

*Chem.* 45, 423-6(1921).—A concd. prepn. of the vitamine from yeast (Osborne and Wakeman, *C. A.* 14, 418) was used. This was treated with sufficient NaOH soln. to neutralize it to litmus and to leave an excess equiv. to a 0.1 *N* NaOH. Portions of this soln. were allowed to stand at 20° and at 90° for varying periods and were then acidified with HCl, evapd. and fed to rats in amts. 25% greater than the minimal requirement of the unaltered prepn. The basic diet was the same in all instances. No difference was observed between the untreated prepn. and that treated with 0.1 *N* NaOH at 20° for 0.5 or 20 hrs., but those portions kept at 20° for 90 hrs. or at 20° for 18 hrs. and then at 90° for 1 hr. were no longer effective. I. GREENWALD

Fermentation of cellulose in the paunch of the ox and its significance in metabolism experiments. AUGUST KROGH AND H. O. SCHMIT-JENSEN. Univ. Copenhagen. *Biochem. J.* 14, 686-98(1920).—The chief object of these expts. was to study the proportion between CO<sub>2</sub> and CH<sub>4</sub> formed by fermentation of cellulose. The original paper must be consulted for details as to methods. "The relation between CO<sub>2</sub> and CH<sub>4</sub> formed by fermentation appears to be independent of the rate of fermentation and, within the limits investigated, of the H-ion concn." The av. CO<sub>2</sub>/CH<sub>4</sub> ratio is 2.6, with extremes in between of 2.2 to 2.9. BENJAMIN HARROW

A method for obtaining uncontaminated specimens of urine from the billy goat; with some notes upon the normal metabolism of this animal. R. A. PETERS. *Biochem. J.* 14, 697-708(1920).—Feces are passed into a bag attached to the goat. The goat urine responds to alterations in the acidity of the diet. The addition of acids to the diet causes the *P<sub>H</sub>* of the urine to decrease, and there is a fall in titratable alkalinity. During starvation, and particularly during the first two days, the urine reaches a decided acid value. BENJAMIN HARROW

Note on the differentiation of the yellow plant pigments from the fat-soluble vitamine. MARJORY STEPHENSON. Biochem. Lab., Cambridge. *Biochem. J.* 14, 715-20(1920).—300 g. of filtered butter fat were dissolved in 1 l. of light petroleum and about 4 g. of fine birch charcoal were added. This was shaken for 2 hrs. in the shaking machine, filtered, and retreated with charcoal. A butter fat free from color was obtained. The petroleum was now distd. off *in vacuo*; the resulting butter was white and resembled lard in appearance. Two sets of 8 rats were put on an exptl. diet (starch, sugar, purified caseinogen, McCollum's salt mixt., fat-free alc. ext. of yeast and 0.5 cc. of lemon juice per rat per day), one set getting the decolorized butter fat, and the other the untreated fat. Perfect growth was maintained in both sets for 8 weeks, after which the expt. was discontinued. Hence it may be concluded that the removal of the coloring matter of butter does not affect the vitamine content. BENJAMIN HARROW

Note on the vitamine content of milk. F. G. HOPKINS. *Biochem. J.* 14, 721-4(1921).—Hopkins' paper (*C. A.* 7, 1373) in which he showed the favorable results obtained by the addition of 2 cc. of milk to a synthetic diet which in itself was insufficient even to maintain rats, has recently been subjected to criticism by Osborne and Mendel (*C. A.* 14, 1702), who claim that more than 2 cc. milk is necessary. Hopkins has now repeated his earlier expts. and confirms them. In 1 of 4 expts., 8 rats were placed upon a synthetic diet. Four received this alone, and 4 were given 2 cc. milk each before receiving their daily feed, great care being taken that the milk was completely consumed. The latter grew vigorously during the 60 days of the expt.; the former grew slowly for about 25 days, when their growth ceased, and on the 35th day 3 out of the 4 died. The other 3 expts. were identical. BENJAMIN HARROW

Effects of heat and aeration upon the fat-soluble vitamine. F. G. HOPKINS. Biochem. Lab., Cambridge. *Biochem. J.* 14, 724-33(1920).—Steenbock, Boutwell and Kent (*C. A.* 12, 2607) and Drummond (*C. A.* 13, 2906) came to the conclusion that

fat-soluble A is readily destroyed by heat. Osborne and Mendel, on the other hand, have recently (*C. A.* 14, 1701) confirmed earlier observations which led to the belief that this vitamin is quite resistive to heat. H.'s paper confirms Osborne and Mendel's work, but in addition it is shown that fat-sol. A is rapidly destroyed by exposure to atm. O at temps. ranging from 15° to 120°. Here is a typical expt.: Two carefully balanced sets of rats were taken, with ten animals in each set. One set received the standard diet with butter previously heated to 120° in the autoclave for 4 hrs.; the other set had the same diet with the butter heated at the same temp. and for the same time, but with simultaneous aeration. (The diet consisted of highly purified caseinogen, potato starch, sucrose, butter and Osborne and Mendel's salt mixt. with the addition of 0.1% KI and a few mg. of NaF. The butter was always first filtered and, however subsequently treated, formed always 15% of the food.) The aeration was carried out in a flask immersed in an oil-bath. By means of a filter pump a stream of air was drawn through the melted fat at the rate of 4-5 bubbles per second. The rats fed on autoclaved milk showed vigorous growth for a period of 70 days, when the expt. was discontinued. No xerophthalmia developed. Those fed on the aerated butter showed a slight growth at first, but then they declined. Three of these rats showed xerophthalmia symptoms on the 40th day, three on the 42nd, three on the 53rd, and one on the 64th day. It is possible that aeration oxidizes fat-sol. A. "Twelve hours' exposure to 120° seems undoubtedly to involve some destruction, but in the absence of air the vitamin is far from being completely destroyed. Butter exposed in thin layers at 15-25° for periods of about a week was found to have lost its power of maintaining the growth or health of rats.

BENJAMIN HARROW

**Researches on the fat-soluble accessory factor (vitamine A). VI. Effect of heat and oxygen on the nutritive value of butter.** J. C. DRUMMOND AND K. H. COWARD. University College, London. *Biochem. J.* 14, 734-9(1920); cf. *C. A.* 15, 252.—This is a confirmation of the work of Osborne and Mendel and that of Hopkins (see preceding abstract).

BENJAMIN HARROW

**Action of ozone on the fat-soluble factor in fats.** S. S. ZILVA. Lister Inst. *Biochem. J.* 14, 740-1(1920).—Cod liver oil exposed for 6-8 hrs. in shallow layers in Petri dishes to the action of the ultraviolet rays is inactivated. That this inactivation is due to the formation of O<sub>3</sub> by the action of the ultraviolet rays obtained from the Hg quartz lamp upon the O of the air was shown by the following expt. The cod liver oil was placed in a layer a few m. thick between 2 tubes, one of which fitted loosely into the other. The outer tube was made of quartz, so that the ultraviolet rays could reach the oil without being previously absorbed. The air above the layer of oil was displaced by CO<sub>2</sub> gas, and the tube was revolved by a water motor during the exposure. An exposure of even 16 hours did not inactivate the oil. On the other hand, light, unlike O, seems to have no effect. A current of O<sub>3</sub> was passed into a dark-stained bottle containing some oil. After 6 hours' exposure the oil was much more viscous than before treatment, and high doses of this modified oil failed to promote growth in rats deficient in the fat-sol. A factor. These results are in agreement with those of Hopkins and Drummond and Coward (see preceding abstracts), except that the action of O<sub>3</sub> is much more drastic than that of O.

BENJAMIN HARROW

**Nutritive value of lard.** J. C. DRUMMOND, JOHN GOLDING, S. S. ZILVA AND K. H. COWARD. *Biochem. J.* 14, 742-53(1920).—Storage of vitamin A occurs in the body fat of the pig, provided the animal receives a diet contg. considerable amts. of this essential (when, for example, the animals are grass-fed). When, however, the diet consists almost entirely of topping and whey, then the body fat shows vitamin A deficiency. During lard manuf. most of the vitamin, if any, is destroyed; the destruction is probably the result of oxidation (see preceding abstracts). The low nutritive value

of lard, then, is due to 2 causes: (1) to a diet offered to pigs which is usually poor in vitamine A, and (2) to the processes of lard manuf.

BENJAMIN HARROW

**Comparative studies on the physiological value and toxicity of cottonseed and some of its products.** ICHÉ G. MACY AND LAFAYETTE B. MENDEL. *Yale Univ. J. Pharmacol.* 16, 345-90(1920).—Cottonseed kernels, alone or mixed with other foodstuffs, are unpalatable and fatally toxic to rabbits, guinea pigs and pigeons, even when fed with molasses and cabbage; and also to albino mice even when the kernels are supplemented with butter fat and inorg. salts. Rabbits and guinea pigs decline rapidly on cottonseed meal; pigeons and mice decline more slowly, depending upon the source and properties of the meal fed; for different samples of cottonseed meal vary greatly in their immediate effects upon animals. The meal was rendered less deleterious and more palatable to rabbits by treatment with moist heat at high temp. Thorough extn. with  $\text{Et}_2\text{O}$  was ineffective in detoxicating cottonseed meal. The decline of animals feeding on cottonseed meal, resulting in the so-called "cottonseed meal injury," is not attributable entirely to inanition. This was demonstrated by determining the food intake of each animal and by conducting control expts.; the latter, in which animals received daily the same quantity of an adequate control diet as that which the cottonseed meal victims consumed, show that death is not the result of starvation, but due to some other factor. Cottonseed meal injury is not due to a lack of water-sol. vitamine; the toxic cottonseed meal contains enough vitamine competely to relieve pigeons suffering from polyneuritis in 2 to 5 days; yeast is ineffective in warding off cottonseed meal injury. Some animals are able to recover from the ill effects of cottonseed diets when the deleterious food is replaced by an adequate diet, others are not. Normal reproduction of albino mice does not take place on a food mixture containing 50% cottonseed meal, 5% butter fat, 4% inorg. salts—a diet which would be regarded as adequate. The second generation tends to be very weak and unable to reproduce in a normal way. The most characteristic clinical symptoms of cottonseed meal injury are emaciation, loss of appetite, weakness, rough hair and unkempt appearance, disturbance in breathing, finally coma and perhaps paralysis.

C. J. WEST

#### ABNORMAL

**Relation of pulmonary infections to the calcium metabolism. Suggestions for a new method of treatment.** G. DELGADO PALACIOS. *Med. Rec.* 99, 475-8(1921).—An exclusive diet of cow milk is a physiol. absurdity because of its high Ca content, and the resultant Ca retention and fecal stagnation. This Ca retention can be inhibited by feeding lime juice simultaneously with the milk diet and increasing the amt. of urine excretion through  $\text{H}_2\text{O}$  ingestion, and feces bulk by cellulose materials. P. believes that influenza and pneumonia are the special diseases that have a chem. basis in abnormal Ca retention and advocates a rapid decalcification by dietary measures in these disorders.

F. S. HAMMETT

#### F—PHYSIOLOGY

ANDREW HUNTER

**Observations on the gases in human arterial and venous blood.** JONATHAN MEAKINS AND H. W. DAVIES. *J. Path. Bact.* 23, 451-61(1920).—Venous or arterial blood was obtained with a 10-cc. glass syringe in which was a small amt. of  $\text{K}_2\text{C}_2\text{O}_4$  and about 1 cc. of sterile paraffin oil. In blood obtained from the radial artery the av. O satn. was 95.3%. There were slight individual variations. The normal arterial  $\text{CO}_2$  content was found to be slightly higher than that calcd. from expts. with defibrinated blood. The breathing of air enriched with O raised the O satn. of arterial blood to 99.2%. Breathing a mixt. containing only 12.6% O lowered the satn. to 81.4%. Rapid shallow breathing in a normal individual lowered the O content of the hemoglobin of the arterial blood. Holding the breath for 40 sec. lowered the

arterial satn. to 83.8%. The rise in  $\text{CO}_2$  was less marked. This indicates that the distress on holding the breath is mainly due to anoxemia. Local temp. conditions caused marked variations in the O content of blood from superficial veins, ranging from complete desatn. to 94.2% satn. Hence methods for the detn. of arterial O content based on calcul. from O content of the venous blood are liable to great error.

JOHN T. MYERS

Contribution to the study of cerebral metabolism by the method of partial circulation. III. Studies of the nature of the materials secreted by the liver which are essential to cerebral function. H. RENAULT-CAPART. *Arch. intern. physiol.* 16, 21-43(1921); cf. *C. A.* 15, 886.—Blood serum contains the elements of the internal secretion of the liver necessary to the functioning of the cerebral centers, since, when an animal in which these centers are out of commission is injected with serum, activity then returns. The role of the red blood corpuscles is apparently limited to the transportation of  $\text{O}_2$ , since when they have been washed and injected into the exptl. animals no stimulating effect is obtained. They are not the carriers of the internal secretion of the liver. The injection of glucose, while it markedly strengthens the force of the heart-beat and reanimates cardiac function, does not cause a restoration of the function of the cerebral centers. Consequently glucose is not the substance in the serum which excites the cerebral metabolism to activity, and the loss of the functions of the central nervous system following the cutting off of the liver from the circulation is not due to the disappearance of the glycogenetic function of the liver. The blood serum of sheep or of cattle has a similar stimulating action on the restoration of the cerebral function as does that of the type of animal under experimentation (dog). Consequently the secreted materials are not specific for the individual species. When the serum that is administered has been previously heated to  $57-60^\circ$  it loses the power to restore the cerebral metabolism, thus demonstrating a high degree of thermolability. This property takes the unknown principle out of the class of the hormones and places it in that of the catalyzers or enzymes.

F. S. HAMMETT

A new working hypothesis concerning the physiological significance of the protamines and the histones in nuclear metabolism. A. CLEMENTI. *Arch. intern. physiol.* 16, 100-18(1921); *Atti acad. Lincei* 29, II, 298-301(1920).—A critical review of the studies made in this field, the main observation of which is that the proteins which are rich in arginine, as the histones and the protamines, are uniquely found in the cell nucleus, that is to say, in the organ destined for the synthesis of nucleic acid, and particularly in the nuclei of the spermatozoa of the cold-blooded animals, in the nuclei of cells destined for the rapid formation of new nucleic acid during cell multiplication following fecundation. This leads C. to the conclusion that arginine is the reserve substance for the synthetic regeneration of nucleic acid during normal cellular metabolism.

F. S. HAMMETT

The significance of the hydrochloric acid of the stomach. L. MICHAELIS. *Biochem. Z.* 111, 105-7(1920).—Polemical with regard to J. Traube (*C. A.* 15, 98).

F. S. HAMMETT

The phosphates of human blood-serum. XII. The phosphorus-distribution according to present methods of separation and isolation. New findings. JOH. FRIGL. *Biochem. Z.* 112, 27-50(1920); cf. *C. A.* 15, 1157.—A review of the amts. of inorg., acid-sol., lipid, protein, total, and residual P of human blood serum as detd. by various workers.

F. S. HAMMETT

Is carbon dioxide pressure or protein swelling the cause of muscle contraction? OTTO FÜRTH. *Biochem. Z.* 113, 42-51(1921).—A polemical reply to Wacker's discussion (*C. A.* 14, 3269) of Fürth's theory of muscle contraction (*Ergebn. d. Physiol.* 17, 363-511(1918)) in which the original argument is adhered to.

F. S. HAMMETT

**Physicochemical studies on body-fluids. II. The condition of the sugar in serum.** STEFAN RUSZNYÁK. *Biochem. Z.* 113, 52-5(1921); cf. *C. A.* 15, 384.—When blood serum and hirudin plasma from pathol. individuals with normal blood sugar content, with hyperglucemia without glucosuria, and with diabetes mellitus, is put through a collodion filter of 7.5% in a Bechhold app. at an  $O_2$  pressure of 10 to 12 atm., only a portion of the blood sugar goes through with the ultra-filtrate. The amt. of sugar retained is apparently independent of the total blood-sugar content. **III. The condition of the residual nitrogen.** S. RUSZNYÁK AND G. HATÉNYI. *Ibid* 56-7.—The residual nitrogen is defined as the non-coagulable nitrogenous portion of the serum. By the same technic as described in the previous paper it was found that the residual N content of the ultra-filtrate is higher than that of the original serum. This is explained by the hypothesis that in protein-containing solns. not all the  $H_2O$  takes part in the soln. of crystalloids, but that there is a "non-solvent" zone. Therefore, in the solvent portion, e. g., in the "dispersion medium" (here the ultra-filtrate) the crystalloids are present in higher concn. than in the whole soln. It is concluded that the residual N of serum is practically all present as crystalloid. F. S. HAMMETT

**Chemical heat regulation of mammals. II. Artificially induced hibernation in mice.** ZOLTÁN ASZÓNI. *Biochem. Z.* 113, 70-88(1921).—The results of this investigation led to the conclusion that the white mouse regulates its body temp. by chem. means at  $19^\circ$  in the fasting and at  $13^\circ$  in the well fed condition. When the animal is put in the cold it falls into a torpid condition with lowered body temp. and metabolism. An increased lowering of the surrounding temp. results in a condition analogous to the winter sleep or hibernation, in which metabolism sinks to  $1/7$  that present in complete chem. regulation. The respiratory quotient falls to 0.7 and if the animal is restored to normal temp. surroundings the condition hardly lasts 24 hrs. When awakening occurs the respiratory quotient rises to higher levels than in the normal conditions. F. S. HAMMETT

**The significance of the abnormal respiratory quotients in hibernation and on awakening from the same.** PAUL HARI. *Biochem. Z.* 113, 89-98(1921).—H. presents several tables of data on the respiratory quotients of animals during hibernation sleep and on coming out of that condition, and expresses the opinion that the lowered exchange during the sleep is due to a marked increase in glycogen formation at this period, which is attended with a notable  $O_2$  consumption. The increased exchange on awakening is naturally on this basis attributed to the burning of the glycogen by the body. F. S. H.

**The distribution of phosphate between the blood-corpuscles and the plasma within and without the organism.** POUZ IVERSEN. *Biochem. Z.* 114, 297-309(1921).—When a soln. of  $Na_2HPO_4$  is added to defibrinated rabbit blood, a certain amt. of the compd. penetrates the corpuscles within the 1st 2 hrs. The increased concn. of "acid-sol. phosphorus" through the addition of salt soln. is always significantly greater in the serum than in the blood corpuscles, and it is to be inferred that the phosphate ions which penetrate the corpuscles retain their characteristics. If a soln. of  $Na_2HPO_4$  is intravenously injected into a nephrectomized rabbit, the concn. of the "acid-sol. phosphorus" in the plasma slowly decreases for several hrs. after the injection. Simultaneously the concn. in the corpuscles rises immediately and can reach very significant values, so that the concn. increase of the "acid-sol. phosphorus" in the corpuscles may be from 2 to 3 times as great as in the plasma. F. S. HAMMETT

**Studies on fibrin coagulation. II. The combined chlorine in blood.** W. FALTA AND M. RICHTER-QUITTNER. *Biochem. Z.* 114, 310-7(1921); cf. *C. A.* 13, 2395.—The observations reported in this paper show that in all serous body fluids and in plasma, but not in serum, the Cl content as detd. by ashing is higher than is found by direct

pptn. These differences are attributed to differences in the dispersion states of the fluids studied, though it is not always proportional to the protein concn. for many transudates and exudates have much "combined" Cl and but little protein. The results are, however, not taken as proof of the presence in the blood plasma of an un-ionized colloiddally dissolved Cl.

F. S. HAMMETT

A note on the relation between the adrenals and the thyroid. GEORGE W. CARR. *N. Y. Med. J.* 113, 389-91 (1921).—C. considers the brain dependent on the adrenals for function and for survival. Studies of the elec. cond. of the cerebrum lead him to the opinion that the body is driven by electricity which is fabricated by the brain cells with the aid of adrenaline. But since the main use of adrenaline is in the emergencies of the moment, the necessity for the const. production and storage of a substance which would increase electric conductance, such as I is known to do, is supplied by the thyroid.

F. S. HAMMETT

Experimental researches on the pituitary body. J. CAMUS AND G. ROUSSY. *Endocrinology* 4, 507-22 (1920).—Expts. are reported on dogs which lead the authors to the conclusions that it is neither the injury to nor the removal of the pituitary body which leads to polyuria in this animal but that rather it is a superficial lesion of the brain that causes the condition. The region injured corresponds to the opto-peduncular space, a lesion in which results in an abundant polyuria much more marked and abundant than can be produced in any other way. These expts. and conclusions are opposed to the opinion that the pituitary is concerned in pathological polyurias. Moreover, genital atrophy as a sequence of hypophysectomy could not be proven. Further expts. failed to show that operative procedures on the hypophysis would produce appreciable alterations in carbohydrate tolerance or alimentary glucosuria nor did the injections of concd. exts. of the posterior lobe, the anterior lobe, or the whole gland sensibly modify—in the animals operated upon—the limit of tolerance to carbohydrates.

F. S. HAMMETT

The relation of the thyroid and of the adrenals to the electric conductivity of other tissues. G. W. CARR. *Endocrinology* 4, 523-6 (1920).—A limited number of observations indicated that an increased conductivity of the brain and liver is an early effect of thyroid feeding. In exhaustion produced by thyroid feeding for prolonged periods the conductivity of the brain is decreased as in exhaustion from other causes. A single dose of adrenaline immediately increases the electrical conductivity of the brain, though the addition of an excessive amt. causes a decreased conductivity. This action of adrenaline is attributed to its influence upon oxidation. It is suggested that the oxidation in the brain cells is the source of the electric energy which is facilitated by adrenaline, and that the passage of the electric energy through the tissues is facilitated by thyreoidin.

F. S. HAMMETT

The influence of the thyroid on the functions of the suprarenals. P. T. HERRING. *Endocrinology* 4, 577-99 (1920).—A comprehensive review.

F. S. HAMMETT

"Ammonia coefficient" of pregnancy. W. C. CULLIS AND E. E. HEWER. *Biochem. J.* 14, 757-61 (1920).—A case is described, which showed a high  $\text{NH}_3$  coeff. (ratio between the  $\text{NH}_3$  and N excreted in the urine), and yet had a successful termination.

BENJAMIN HARROW

Physiological output of the marching soldier. A. D. WALLER AND (MISS) G. DE DRACKER. *Bull. acad. roy. méd. Belg.* [4] 30, 1049-56 (1920).—Energy expended in marching can be measured by the vol. of  $\text{CO}_2$  expired over a 50 meter course, this being approx. 0.1 cc. per kg. per horizontal meter. A soldier, wt. 72 kg., carrying 28 kg. and marching at the rate of 1.33 m. per sec. (4 km. per "hr." of 50 min.) expends about 250 calories per "hr.," or 1000 calories in 4 "hrs." over a flat course of 16 km.

M. HEIDELBERGER



**Respiratory insufficiency at very high altitudes and its correction by subcutaneous injections of oxygen.** RAOUL BAYRUX. *Compt. rend.* 172, 291-4(1921); cf. *C. A.* 14, 1151.—The respirations per min. were counted, the vol. per respiration was measured and the vol. of air breathed per min. computed *before* and *after* subcutaneous injections of O<sub>2</sub> [dose not stated] at Paris, at Chamonix (altitude 3000 m.) before ascending to the observatory, at the observatory on Mt. Blanc (altitude 4350 m.), and at Chamonix on descending. The results reduced to 0° and 760 mm. are given in the following table in the order above mentioned, the first horizontal line showing respirations per min., the second line liters of air per respiration, and the third liters per min.

Paris.		Chamonix.		Mt. Blanc.		Chamonix.	
Before.	After.	Before.	After.	Before.	After.	Before.	After.
17.0	16.6	18.2	16.4	19.8	17.6	18.2	14.4
0.79	1.09	0.64	0.85	0.44	0.58	0.99	1.37
13.43	18.09	11.65	13.94	8.71	10.71	18.02	19.73

The respiratory flow diminishes absolutely as the altitude increases. At all altitudes the subcutaneous injection of O<sub>2</sub> corrected the progressive insufficiency of the respiratory flow.

L. W. RIGGS

#### G—PATHOLOGY

H. GIDEON WELLS

**The effect of osmic acid and other agents on the affinity of receptors for immune bodies and their antigenic properties.** M. KOSAKAI. *Japan. J. Path. Bact.* 23, 425-42(1920).—The effects of heat, alc., HCHO, ether, acetone, H<sub>2</sub>O<sub>2</sub>, and saponin on the receptors of red blood cell stromata were examd. All except saponin cause clumping of the stromata, which is accompanied by a decrease in the power of fixing specific immune bodies. The latter effect may be due in part to the diminution of surface. The brown fluid which remains when a suspension of heated red cells has had the acid parts centrifuged out contains no demonstrable receptors. Stromata treated with osmic acid will remove not only homologous immune bodies from serum but will remove receptors for which untreated stromata have no affinity. Boiled stromata which have almost lost their power of fixing homologous immune body will regain this power when treated with osmic acid. Stromata treated with osmic acid will remove bacterial agglutinin but may fail to remove hemagglutinin. Treatment with osmic acid will confer similar properties on an emulsion of guinea-pig liver. Osmic stromata which have been treated with immune bodies do not part with the latter when brought into contact with normal homologous red cells at 37°, or when heated with a soln. of cane sugar at 55°. Estn. of the loss of N occurring when immune serum is treated with stromata does not explain the loss of immune bodies. The action of osmic stromata on immune serum is not due to diffusion from the stromata of traces of osmic acid or other substances.

JOHN T. MYERS

**The stalagmones.** H. BECHOLD AND L. REINER. *Inst. f. Kolloidforschung*, Frankfurt, a/M. *Munch. med. Wochschr.* 67, 891-2(1920).—Substances which diminish the surface tension of the urine are called stalagmones. Expts. with ultrafiltration on various urines show that more than one substance enters into consideration. The stalagmones are colloids or semicolloids of different degrees of dispersion, easily sol. in water, amphoteric or acid, very stable and well absorbable. To the stalagmones belong first of all protein-cleavage products like oxyproteic acids, albumoses, peptones; in certain diseases proteins and bile constituents. The stalagmones are responsible for the more rapid sedimentation of the red blood corpuscles which occurs in the citrate plasma of certain diseases.

S. AMBERG

**Antibody studies. I. Reversal of the antigen-antibody reaction.** F. M. HUNTER. *Milford Bldg. Labs. J. Immunol.* 6, 117-22(1921).—The assumption seems less

reasonable that the antibodies are attached to antigen in 2 distinct portions in sharply different degrees of firmness than that a graduated variability in the firmness of the union exists and that those antibodies which are less firmly bound are the first to be dissociated. Although complete reversal of the antigen-antibody reaction may be impossible there is abundant proof of the possibility of an incomplete or partial reversal enabling the production of antibody solns. in a more or less pure state. II. The recovery of antibody from sensitized antigens: technic. F. M. HUNTOON AND S. EYTRIS. *Ibid* 123-84.—At present the most that can be safely said of the phenomenon of dissociation of the antigen-antibody combination is that apparently it is governed by the diln. of the "binding salt" present, and that the nature of this "binding salt" differs for different antibodies. In any case, the conception of such "binding salts" offers a different angle from which to attack the problem of the nature of the antigen-antibody combination. A theory based on the assumption that diln. of the "binding salt" is responsible for the reversal of antigen-antibody combinations and that such "binding salts" differ for different antibodies will explain many of the facts noted in such dissociation work. Several examples are cited. As a practical application of the exptl. work, sterile exts. of the pneumococcus protective antibody have been produced approximating in antibody content the best immune sera, and containing so low a serum protein content that 5 cc. amts. sensitized guinea pigs only irregularly to subsequent injections of horse serum. III. Chemical nature of antibody. F. M. HUNTOON, P. MASUCCI AND E. HANNUM. *Ibid* 185-200.—See C. A. 15, 703. E. B. FINK

Experiments with the flocculation test (Sachs-Georgi) for syphilis. W. R. LOGAN. Edinburgh. *Lancet* 1921, I, 14-6.—Under the conditions of these expts. results can usually be obtained with the flocculation test which closely approximate those of careful Wassermann tests. Until the factors which cause false reactions are definitely recognized and can be controlled, the test should not be used to supplant the Wassermann reaction, although it may profitably be used as an additional control. E. B. FINK

The neurological aspects of shock. FREDERICK MOTT. London. *Lancet* 1921, I, 519-22.—It may be presumed that in anaphylactic shock there is a disturbance of the static equilibrium of all the cells of the body, esp. of the nervous system, and the term colloidoclasia would more accurately represent the condition. Idiosyncrasy may be regarded as a specialized inherent hypersensitiveness to disturbance of the static colloidal equilibrium from the action in the body of particular substances. A somewhat similar disturbance may be the explanation of commotional shock, in which no sufficient macroscopic or microscopic changes can be found to account for the symptoms. Study of the living neuron shows that Nissl bodies and fibrils in the ganglion cells are artefacts, the result of death changes, and due to the action of fixatives and stains; for if the living nerve cell be examined by direct illumination, it appears as an emulsion of black dots in the plasm, in the center of which is the nucleus; the converse is observed in the cell when examined microscopically. When the living cells are stained with vital blue the granules take the blue stain. If the cells so stained are kept in cerebrospinal fluid in an atmosphere of N the blue color fades to green. This affords evidence that the granules form an O<sub>2</sub> surface like spongy Pt. By the catalytic action of the P and Fe of the nucleus, the mol. O<sub>2</sub> on the surface of the granules is continually being converted into at. O, and this process is fundamental to the life and functional activity of the neuron. It is conceivable that a violent commotion, even without contusion sufficient to cause minute hemorrhages into the nervous substance, may have a profound effect upon these delicate colloidal structures and cause a disturbance of static equilibrium.

E. B. FINK

Experimental study of the action of normal beef serum in anthrax infection. R. KRAUS AND BELTRAMI. Buenos Aires. *Z. Immunol.* 31, 93-107(1921).—Exptl.

evidence is furnished that normal beef serum is useful in the treatment of anthrax infection, and has the same effect as anthrax-immune serum. E. B. FINK

**Experimental study of the action of normal beef serum in diphtheria.** R. KRAUS AND A. SORDELLI. Buenos Aires. *Z. Immunität.* 31, 107-24(1921).—The use of Behring's diphtheria serum is the only rational treatment and there is no evidence for antitoxin therapy of diphtheria with normal horse serum. The latter was proved by animal expts. to possess a certain amt. of protective antitoxin action. E. B. FINK

**The reactivation of complement by acids and alkalis.** HANS SCHMIDT. London. *Z. Immunität.* 31, 125-36(1921).—Expts. showed that the addition of alkali to a complement end-piece obtained by the treatment with  $\text{CO}_2$  could not induce a hemolytic action of the original serum upon sensitized corpuscles as long as isotonicity of the soln. is maintained. A certain amt. of lysis is observed in hypertonic solns., but this is not due to a sp. action of the end-piece but is a result of osmotic disturbance. Similar results were obtained with HCl. Heat-inactivated complement and end-piece could not be reactivated by the addition of either acid or alkali. The same was true of a complement inactivated by shaking. E. B. FINK

**The action of heavy metals on red blood cells.** W. SCHÜRMANN AND TR. BAUMGÄRTEL. Giessen. *Z. Immunität.* 31, 151-60(1921).—Cu in the form of  $\text{Cl}$ ,  $\text{SO}_4$  and acetate ppts. normal and sensitized beef and sheep corpuscles.  $\text{CuSO}_4$  and Cu acetate agglutinate sensitized more actively than normal cells, while  $\text{Cu}(\text{NH}_4)\text{Cl}_2$  ppts. only normal washed sheep and beef cells. Ni in the form of chloride, nitrate, sulfate and acetate ppts. only sensitized sheep cells.  $\text{FeCl}_3$  ppts. normal beef and sheep cells. Sensitized beef, but not sheep, cells are more actively clumped by  $\text{FeCl}_3$  than normal cells. Beef and sheep cells, normal and sensitized, exhibit differences in sensitivity to the action of Cu, Ni and Fe salts. The great variability of action indicates that 2 factors are concerned: one, due to differences in species, the other, the pptg. action of the individual electrolytes which depends upon the degree of dissociation of the metallic salts. E. B. FINK

**The "dry drop" seroscopic (colloidoscopic) method.** HERMANN DOLD. Halle. *Z. Immunität.* 31, 161-9(1921).—A drop of colloid-crystalloid mixt. placed upon a cover glass or hanging drop slide and allowed to dry rapidly, reveals an interesting picture when examined with the dry lens. If a large number of drops are prepd. in a similar way from the same fluid the picture is not identical in all but they closely resemble each other and have the same general structural character. The "dry drop" when properly prepd. is an indication of the composition of a colloid-crystalloid fluid. The method may be used as a seroscopic aid to the study of structural changes in sera and other body fluids. As a practical application of the method, the results of a Wassermann reaction may be preserved by the "dry drop" method and used for future reference. E. B. FINK

**Fat studies.** HANS MÜCH AND HANS SCHMIDT. Hamburg. *Z. Immunität.* 31, 169-200(1921).—Guinea pigs and rabbits were injected parenterally with animal and vegetable fats. Sp. antibodies against these fats could not be demonstrated either by the local sensitization test (Wheal formation) or complement fixation. Injection of proteins of the animal or plant from which the fat was derived either before or together with the fat, did not lead to the production of antibodies against the fats. Attempts to demonstrate the presence of a substance in the serum of treated animals which would produce sp. pptn. in fat emulsions yielded indefinite results. The reaction of human serum with an emulsion of human fat is inconstant and irregular. There must be a difference between bacterial and other fats, since the former are able to stimulate antibody production. Neutral fats of plant and animal origin are of simple mol. struc-

ture, can be readily destroyed in the body by lipases, and antibody formation against them is not necessary. E. B. FINK

**Anticomplementary action of equine sera.** R. MANNINGER. Budapest. *Z. Immunität*, 31, 222-48(1921).—The anticomplementary action of horse, mule and ass sera is a function of their globulin content. The degree of anti-complementary action is not detd. by the abs. quantity of globulin in the serum, but by the relation of albumin to globulin (protein quotient). The lower the protein quotient of a given serum the greater is its anticomplementary action and the higher the temp. necessary to inactivate that serum in complement fixation expts. Horse serum is easily inactivated (55°). Equine sera are anticomplementary because their degree of dispersion furnishes optimal surfaces for the production of adsorption phenomena. The globulins adsorb a certain portion of the complement end-piece. Inactivation of sera is due to a reaction of globulins with H<sub>2</sub>O whereby the globulins originally in the form of dispersoids become emulsoids and lose their complement-adsorbing property. Coagulated globulin fractions in sera heated to 65° are not anticomplementary because their sp. surfaces do not fulfill the necessary conditions for adsorption. E. B. FINK

**Nature of the Wassermann reaction.** FRITZ M. MEYER. Berlin. *Z. Immunität* 31, 278-83(1921).—The presence of a sp. component in the Wassermann reaction is a possibility but cannot be proved by existing exptl. methods. E. B. FINK

**Increase of agglutinin titer after bleeding.** OTTO OLSEN. Freiburg. *Z. Immunität* 31, 284-90(1921).—The expts. of Langer indicating that daily bleeding caused an increase in agglutinin were not confirmed. The increases depend upon individual variations in animal and exptl. conditions about which we have little present knowledge. E. B. FINK

**Increase of antibody (agglutinin) after bleeding.** HANS LANGER. Charlottenburg. *Z. Immunität*. 31, 290-2(1921).—Repetition of previous expts. gave similar results, i. e., an increase in agglutinin titer in 2 of 6 animals following daily bleeding. Polemic. E. B. FINK

**The antigenic function of the blood platelets.** PAUL GOVAERTS. Arch. intern. physiol. 16, 1-20(1921).—See C. A. 14, 1852. F. S. HAMMETT

**Fibrin-enzyme and fibrinogen determination after injection of normal sera into normal animal bodies.** T. TOGAWA. Biochem. Z. 109, 25-42(1920).—Dogs, rabbits, and guinea pigs were used as control and exptl. animals, while the sera to be tested were obtained from rabbits, dogs, guinea pigs, pigs, sheep and cattle. Mg and oxalate plasmas were used and the standard sera and plasma were always dild. 1:10 immediately before the expt. Administration was intravenous. Samples for testing were taken immediately after injection, and at 15, 30, 60, 120 and 180 min. thereafter. In general, after the injection of serum into the normal animal an increased fibrinogen content was observed, which was almost const. when auto-serum or serum from the same species was used. This increase in fibrinogen content followed immediately after the injection or 15 min. thereafter and lasted at the most for 15 to 30 min. Apparently the fibrinogen-increasing activity is a specific power of animal serum which cannot be destroyed by usual protein preps. or other reagents. F. S. HAMMETT

**Studies with antigens and antibodies on the surviving artificially perfused liver.** II. Studies with tetanus toxin. M. HAHN and E. v. SKRAMLIK. Biochem. Z. 112, 151-63(1920).—These studies were made on the guinea pig liver by the method previously described (cf. C. A. 14, 2380), using a desiccated tetanus toxin sufficient to kill a 20-g. mouse in 4 days in a concn. of 10<sup>-6</sup> g. Tetanolysin has a great affinity for liver tissue, is bound by this organ and cannot be removed by massive perfusion with its antitoxin. The measure of this affinity of the toxin for the body cells is significant from the fact that only a great excess of antitoxin in the toxin-antitoxin mixt. can prevent the

tying up of the former by the tissues. This fact is of particular interest, since it confirms in a new manner the old finding that only large doses of antitoxin are able to inactivate the toxin in the body. Even when the lysin is in the wound-up condition it is able to exert a deleterious action on other body cells. Red-blood cells are agglutinated and after a time dissolved when passed through such a liver. The attachment then does not mean that a detoxication has occurred. Tetanospasmin also is held in significant amts. by the liver tissue, and the elective ability of this organ to attract and hold the toxin shows anew the division of the tetanus toxin into 2 different components.

F. S. H.

**Liver function under experimental pathological conditions.** W. LÖFFLER. *Biochem. Z.* 112, 164-87(1920).—L. poisoned the exptl. animals with P or the isolated surviving liver with alc.,  $\text{CHCl}_3$ , nicotine, and KCN and measured the changes in the capacity of the organ for urea formation on isolation and perfusion. P poisoning had no injurious effect on the ability of the liver to form urea when perfused with ammonium salts unless the animals were killed as the result of the poisoning. The addition of 5.5% of alc. to the perfusion fluid did not disturb the capacity of the liver to form urea within the following  $\frac{1}{2}$  hr. Even when 11% of alc. was present there continued to be a marked urea formation during this time period. Severe injury to the liver by alc., however, inhibited urea formation. The addition of  $\text{CHCl}_3$  in small amts. to the perfusing fluid had no effect; larger doses were inhibitory. Nicotine in 0.01% concn. was ineffective. KCN in 0.002% soln., in the system liver and perfusing fluid, completely prevented urea formation. This loss of function was restored by washing the organ clear of the toxic substance. These results lead L. to conclude that urea formation in the surviving liver is based on the fact that cell structure is not destroyed.

F. S. HAMMETT

**Serum hemolysis and lipolysis.** O. OLSEN AND K. GOETTE. *Biochem. Z.* 112, 188-202(1920).—The results indicate that there is no relation between the amt. of hemolytic amboceptor and blood-lipase content of the blood serum as investigated, though there did occur some evidence that there was a certain agreement between the total complement content and the lipase amt. in some cases. In many expts. it was possible always to detect the presence of lipase in that portion of the serum containing the end-piece, while in the middle-piece sediment it was never found, and hemolysis was never found to occur without the presence of lipase being detected. The hypothesis is advanced that the lipoids of the red blood corpuscles present in previously unweakened condition are subjected to the lipolytic action of the end piece by mixing of the amboceptor and the middle-piece and hence hemolysis follows.

F. S. HAMMETT

**Studies on protein reactions. IV. The physical chemistry of agglutination.** A. v. SZENT-GYÖRGYI. *Biochem. Z.* 113, 36-41(1921); cf. *C. A.* 15, 376, No. 1537.—S. studied here the effect on the agglutinins of passing a current of electricity through horse-sera of original titers of 20,000 and 200,000; 1 cc. and 0.1 cc. of the sera, respectively, were used for the test and dild. with various buffer solns. of  $\frac{1}{20}$  M concn. After the current had been passed through the mixt. for 3 or 4 hrs. the solns. at each pole were removed, neutralized to  $p_H = 7$ , and the titer of their agglutinin content was made in the usual way. The isoelectric point of the agglutinins lay between  $2.10^{-8}$  and  $4.10^{-8}$   $p_H$ ; the titer at  $1.10^{-8}$  was over 64 at the anode and 0 at the cathode, while the titer at  $1.10^{-4}$  was over 64 at the cathode side and 0 at the anode.

F. S. HAMMETT

**Chemical and biochemical studies of the nervous system in normal and pathological conditions. VIII. The chemical composition of the brain in dementia precox.** G. FIGINI. *Biochem. Z.* 113, 231-45(1921).—P. reports the chem. analysis of 8 brains from cases of dementia precox in different phases of the disease. The results, as a whole, when compared with the normal show an increase in the  $\text{H}_2\text{O}$  content, a cholesterol content that is normal or a bit above, decrease in unsatd. phosphatides varying

from 20 to 35%, a noteworthy decrease in the satd. phosphatides, cerebrosides, sphingolactoside, etc., of about 50%, and an apparent percentage increase of protein residue.

F. S. HAMMETT

**Studies on phyto-hemagglutinin.** V. K. RUSS AND E. ORSTERLIN. *Biochem. Z.* 114, 268-76(1921).—The soy bean—*Glycine hispida*—and other legumes contain substances which exert an agglutinating action on the blood corpuscles of various species of animals. The extn. of the active hemagglutinating principles from legumes is quite dependent on the degree of the mechanical fineness of the material used. These hemagglutinins are only slightly thermolabile, since at a temp. of 60° there is no loss of activity in 15 min.; at 80° for 15 min. the destruction, however, is marked and at 100° for 5 min. the activity is completely lost. The substances are pptd. by  $(\text{NH}_4)_2\text{SO}_4$  and EtOH but are not extd. by  $\text{Et}_2\text{O}$  from the original product. It is possible to immunize animals with such active exts. and to obtain an immune serum which has a sp. anti-hemagglutinating action against the homologous ext.

F. S. HAMMETT

**Treatment of asthma by vaccine therapy.** J. MINET. *Bull. mem. soc. med. hop. Paris* 37, 106-12(1921).—M. prepd. auto-vaccines from the flora of the pulmonary tree, though it was impossible to reproduce by culture the exact proportions of the micro-organisms originally present. Treatment with such preps. was efficacious in about 60% of the cases studied.

F. S. HAMMETT

**Digestive vaccine therapy in twenty-one cases of typhoid fever.** L. BLAYE. *Bull. mem. soc. med. hop. Paris* 37, 113-5(1921).—The treatment of typhoid fever by very small doses of auto-vaccines gave satisfactory results.

F. S. HAMMETT

**Azotemia and digestive hemoclasia in gastric ulcer.** P. LE NOIR, CHARLES RICHT, JR. AND A. JACQUELIN. *Bull. mem. soc. med. hop. Paris* 37, 121-6(1921).—Since the blood urea was detd. in these 38 cases of gastric ulcer by the hypobromite method, the value of the figures is questionable.

F. S. HAMMETT

**Variations in the amount of glucose, albumin and urea in the cerebrospinal fluid of general paresis.** MARCEL BRIAND AND A. ROUQUIER. *Bull. mem. soc. med. hop. Paris* 37, 145-6(1921).—The examn. of 50 cases of general paresis showed that the glucose content of the cerebrospinal fluid usually remains within normal limits and when it is increased is below that found in other pathol. conditions. Increased albumin was, of course, present in all cases and frequently went over 1 g. The upper limits ranged between 1.10 and 1.20 g., the lower between 0.5 and 0.6 g. The urea content of the 5 cases tested was around 0.5 to 0.6 g. The chem. modifications of the cerebrospinal fluid are not coincident with the periodical changes observed clinically.

F. S. HAMMETT

**The skin reaction to tuberculin during menstruation and after ovariectomy.** E. COULAND. *Bull. mem. soc. med. hop. Paris* 37, 155-9(1921).—At the beginning of menstruation the cutaneous response to tuberculin is inhibited; it also tends to disappear after castration.

F. S. HAMMETT

**Coagulation disturbances in erythemia.** CH. LAUBRY AND E. DOUMER. *Bull. mem. soc. med. hop. Paris* 37, 170-4(1921).—The coagulation time of the blood from cases of erythemia is markedly prolonged. This is considered to be due to the presence of a pronounced fibrinolysis occurring in the disorder.

F. S. HAMMETT

**Anti-seral medication by sodium carbonate intravenously injected.** SICARD AND PARAF. *Bull. mem. soc. med. hop. Paris* 37, 229-32(1921); cf. C. A. 15, 1162.—The preliminary intravenous injection of  $\text{Na}_2\text{CO}_3$  suffices to prevent the not infrequent toxic effects of the injection of sera from various sources used for prophylaxis or treatment. It is efficacious when used in solns. of 2.5% strength made of c. p.  $\text{Na}_2\text{CO}_3$  plus 9 mols.  $\text{H}_2\text{O}$  of crystn.

F. S. HAMMETT

**Studies on the colloidal benzoin precipitation reaction in cerebrospinal fluids.** E. DUHOT AND P. CRAMPON. *Bull. mem. soc. med. hop. Paris* 37, 807-10(1921).—A continuation of studies on this reaction with more extensive applications. Negative results were obtained in non-syphilitic cases. In general paralysis practically constant positive results were obtained, and in neuro-syphilis 84% of the tests gave positive reactions. The opinion is expressed that the reaction is more sensitive than the Bordet-Wassermann.

F. S. HAMMETT

**The classical endocrine syndromes.** L. F. BARKER. *N. Y. Med. J.* 113, 353-63 (1921).—A succinct review of the clinical syndromes which can be attributed to disturbances of function of the thyroid, parathyroids, thymus, hypophysis, pineal, adrenal and gonad glands.

F. S. HAMMETT

**Suggestions regarding the role of the hypophysis in Grave's disease and myxedema.** G. A. FRIEDMAN. *N. Y. Med. J.* 113, 370-4(1921).—Since the hypophysis seems to show histological changes in Grave's disease similar to those found in hyperpituitarism, and in myxedema to those in hypopituitarism it is evident that there is a certain degree of hypophyseal hyperactivity in hyperthyroid, and of hypoactivity of the pituitary in hypothyroid states. This leads to the idea that the increased metabolic rate (especially emaciation), the tendency of glucosuria and the abnormal skeletal growth as signs of Grave's disease may be attributed in part to hypophyseal overactivity; while the decreased metabolic rate (adiposity), high sugar tolerance and retardation of epiphyseal closure of myxedema can be attributed to pituitary underactivity.

F. S. HAMMETT

**Hypothyroidism and tabes dorsalis.** SMITH ELY JELLIFFE. *N. Y. Med. J.* 113, 363-6(1921).—J. cites several cases from his experience which gave the usual syndrome of tabes dorsalis with negative Wassermann. Suspecting hypothyroidism, thyroid administration was begun with the result that the condition was alleviated.

F. S. H.

**Injurious action of carbon dioxide on red blood corpuscles.** W. PATZSCHKE. *Z. physiol. Chem.* 109, 1-11(1920).—Expts. *in vitro* show that  $\text{CO}_2$  increases by 50 or 100 times the action of inorg. blood poisons which form methemoglobin, the incidence of the reaction being accelerated markedly by rise of temperature. In presence of aniline or nitrobenzene, the formation of methemoglobin in human blood occurs only after introduction of  $\text{CO}_2$ . It is therefore probable that the development of the action of certain poisons in the veins is brought about by the  $\text{CO}_2$  present. Intensification of the formation of methemoglobin by  $\text{CO}_2$  is produced, not only in suspensions, but also in solns. of blood corpuscles and in hemoglobin solns., so that it may be assumed that the  $\text{CO}_2$  induces changes in the hemoglobin favorable to the formation of methemoglobin. Blood corpuscles charged with  $\text{CO}_2$  are labile cells readily accessible to injury, whereas O protects the corpuscles.

J. C. S.

**The biology of silicic acid, alumina and iron.** M. GONNERMANN. *Z. physiol. Chem.* 111, 32-5(1920).—The Si, Al and Fe contents of a selection of gallstones, intestinal, kidney, bladder and cancer concretions, and benzoar-stones, were detd.

J. C. S.

**Sex difference in the presence of natural hemolysin in the rat.** Y. SUZUKI. *Wistar Inst. of Anat. and Biol. Am. J. Physiol.* 53, 483-7(1920).—Natural anti-pig hemolysin is not usually present in the serum of younger albino rats. In older rats it may be present, more frequently in the female than in the male. In females it is not only more active but the proportion of cases is far greater during pregnancy, as well as during the first week after parturition. In cases of lung infection the number of cases in which the anti-pig hemolysin is present in males tends to increase.

J. F. LYMAN

**Effect on the composition of the blood of maintaining an increased blood volume by the intravenous injection of a hypertonic solution of gum acacia and glucose in**

**normal, asphyxiated and shocked dogs.** H. L. WHITE AND J. ERLANGER. Washington Univ. *Am. J. Physiol.* 54, 1-29(1920).—A strongly hypertonic soln. (18% dextrose and 25% acacia) was injected intravenously into dogs at the rate of 5 cc. per kg. per hr., the injection lasting 1 hr., and the resultant changes in blood vol. and composition were studied. In normal and asphyxiated animals the immediate effect was a marked increase in blood vol. with a gradual fall, but not a complete return to normal after several hrs. The absolute plasma protein is increased slightly or not at all. There is a marked hyperglucemia immediately after the injection which is accentuated by morphine and asphyxia. The blood sugar falls to or nearly to normal within 2 hrs. There is only a trace of sugar excreted by normal animals, except when morphine or asphyxia cause marked glucosuria. The Cl concn. of the plasma does not return to normal for several hrs. The non-protein N of the plasma remains constant, indicating an easy entrance of urea into the plasma from the tissues. The crystalloid osmotic pressure of the plasma does not remain constant. In shocked animals the blood vol., markedly diminished by shock, is increased to above the normal level by the injection and then it gradually falls to or below normal. The amount of plasma protein, markedly diminished in shock, is increased by the injection and the increase continues for some time. It is believed that at least a part of the increase in plasma protein is due to a passage of protein in through the vessel walls. Gum acacia seems to take the place of plasma protein in holding  $H_2O$  in circulation.

J. F. LYMAN

**The alkaline reserve of the blood of the insane.** N. SURTSU. Wistar Inst. *Am. J. Physiol.* 54, 147-52(1920).—The alk. reserve (as measured by the amt. of  $CO_2$  in the blood plasma combined as bicarbonate) of the insane appears to fall within the limits considered normal for healthy persons. There were no demonstrable differences in the absolute amts. of alk. reserve of the bloods from excited or depressed patients. The variability of the plasma  $CO_2$  combining capacity seems to be higher in the insane than in the small group of normals studied.

J. F. LYMAN

**The respiratory mechanism in cardiac dyspnea. I. The low alveolar carbon dioxide of cardiac dyspnea.** J. P. PETERS, JR. AND D. P. BARR. Russell Sage Inst. of Pathol., Bellevue Hosp. and Cornell Univ. Med. College. *Am. J. Physiol.* 54, 307-34(1920).—Alveolar  $CO_2$  was detd. in normal and in cardiac patients with dyspnea using (1) the Haldane method, (2) the Plesch method, and (3) the Henderson-Laurens method. By the Haldane method, patients with cardiac decompensation show a low alveolar  $CO_2$  in comparison with the  $CO_2$  capacity of the venous plasma. The level to which alveolar  $CO_2$  can rise under the influence of rebreathing is proportionally reduced. The Plesch method and the Henderson-Laurens method give results for alveolar  $CO_2$  somewhat lower in decompensated cardiac subjects than in normal persons; but high in relation to the values given by the Haldane method. **II. The effective lung volume in cardiac dyspnea.** *Ibid* 54, 335-44. In cardiac patients with dyspnea there is no evidence of an increased residual air. The vital capacity is diminished; hence the effective lung vol., i. e., vol. of air in lungs available for the exchange of gases, is reduced. **III. The effective ventilation in cardiac dyspnea.** *Ibid* 54, 345-54. The min. vol. of effective or exchange air is increased during cardiac decompensation. This greater effective ventilation is necessitated by the low concn. of  $CO_2$  in the exchange air. Great increases in ventilation are impossible because of the diminished effective lung vol. of decompensated cardinals.

J. F. LYMAN

**Studies in diabetes. Series II. The internal pancreatic function in relation to body mass and metabolism. 5. The influence of fever and intoxication.** F. M. ALLEN. Rockefeller Inst. Med. Research. *Am. J. Physiol.* 54, 375-81(1920); cf. *C. A.* 15, 1036.—The aggravation of human diabetes is a reaction to intoxication rather than to fever, as shown by its occurrence in the afebrile stage of tuberculosis and by



other evidence. Infection and fever have no specific influence in diminishing or aggravating the diabetic tendency in dogs. 6. Gas bacillus infections in diabetic dogs. MARY B. WISHART AND IDA W. PRITCHETT. *Ibid* 54, 382-7.—Intramuscular injections of *B. aerogenes capsulatus* produced local necrosis and gas formation in partially depancreatized dogs. There did not seem to be any lowering of resistance in these animals due either to diabetes itself or to excess of dextrose in the body fluids. A lowering of tolerance by infection was demonstrable both by feeding and by intravenous dextrose tests. Though this influence is less in animals than in human patients, the difference seems to be one of degree rather than of kind. J. F. LYMAN

Experimental traumatic shock. I. The basal metabolism. J. C. AUB. Harvard. *Am. J. Physiol.* 54, 388-408(1920).—Shock in cats under urethane anesthesia was produced by crushing the thigh muscles. Exptl. traumatic shock causes a fall in the rate of basal metabolism (measured by respiratory exchange) to 70% of the original level. The degree of fall is dependent upon the severity of the shock produced. A similar fall in metabolic rate may be rapidly produced by interfering with the circulation by increased pericardial pressure. The effect of hemorrhage is not const. Recovery from shock after blood transfusion is usually associated with a prompt return of the metabolic rate to the normal level. II. The oxygen content of blood. J. C. AUB AND D. CUNNINGHAM. *Ibid* 408-15.—There is a markedly diminished  $O_2$  content of the venous blood in exptl. traumatic shock. This change occurs before the blood pressure falls to a shock level, and is still present after apparent recovery from shock. The blood flow is also greatly decreased in the development of, during and after shock. The resulting anoxemia of the tissues may be the cause of the decreased metabolism accompanying shock. III. Chemical changes in the blood. J. C. AUB AND H. WU. *Ibid* 54, 416-24.—Animals with marked muscle trauma but without true shock showed only slight changes in total non-protein N, urea, creatine and sugar of the blood. These constituents, especially the creatine and sugar, rose markedly as shock developed. In control animals the detd. constituents showed no appreciable change. The marked rise of creatine is direct evidence of the presence in the blood of products of muscle necrosis, and is therefore suggestive evidence of the theory of the chem. cause of traumatic shock. J. F. LYMAN

The testing of diphtheria toxin and antitoxin by intracutaneous injection into guinea pigs. A. T. GLENNY AND K. ALLEN. *J. Path. Bact.* 24, 61-3(1921).—Very small fractions (about 1/500th) of a fatal dose of toxin will produce an intracutaneous reaction. This reaction is a well defined red area about 15 mm. in diameter at the end of 36 hours. The smallest amt. which will produce the reaction is called the "Minimal Reacting Dose" or M. R. D. It is specific and is prevented by antitoxin. It is probably an index of the toxin without the toxoid content. The antigenic power of a toxin can be measured by its combining value with antitoxin. The standard for toxin is the limiting dose of toxin which produces the above reaction when injected together with 1/500 of a unit of antitoxin. It is termed the Ln/500 dose or the "skin test dose." It agrees well with the subcutaneous method. JOHN T. MYERS

Observations on the gases in human arterial blood in certain pathological pulmonary conditions, and their treatment with oxygen. JONATHAN MEAKINS. Univ. Edinburgh. *J. Path. Bact.* 24, 79-90(1921).—It seems probable that the respiratory center along with other nervous reflexes is kept in a sensitive condition through a certain degree of anoxemia produced during the sleeping hours. The organism can adapt itself to a considerable degree of anoxemia. A lowering of the blood O satn. is found in cases of asthma, chronic bronchitis, and emphysema without producing great distress, which would lead to pronounced cardio-vascular and nervous disturbances if produced suddenly. There is a marked lowering of the arterial blood O in pneumonia, which is

sudden and constant. This probably produces many of the grave symptoms. In three cases of pneumonia the symptoms were relieved by the administration of O. In four cases of lobar pneumonia the CO<sub>2</sub> content of arterial blood varied between 42 and 44 vol. %. This is probably due to the increased pulmonary ventilation. J. T. MYERS

**Studies in diabetic acidosis.** E. G. B. CALVERT, E. B. C. MAYRS AND T. H. MILROY. *J. Path. Bact.* 24, 91-116(1921).—The excretion of alkali is increased in diuresis. Variations in alkali output follow alterations in vol., but are less marked. The percentage of N excreted as NH<sub>3</sub> is reduced in diuresis. The relative NH<sub>3</sub> curve may reproduce variations in the reaction curve with considerable accuracy. Vol. reaction, NH<sub>3</sub>-N, total acid and alkali output remain more const. in acidosis than in health, high acidity and NH<sub>3</sub> output being very characteristic of acidosis. In diabetic acidosis the alkali tide shown in the normal individual by a fall in the monobasic phosphate value and in the NH<sub>3</sub> output during the second hour after rising from bed is not observed. Also a very much larger dose of bicarbonate or citrate is required to affect the reaction or NH<sub>3</sub> output of the urine. The first effect of the NaHCO<sub>3</sub> in the acidosis case is upon the NH<sub>3</sub> excretion; the fall of monobasic phosphate value comes later. In the case of a corresponding dose of citrate in the same person both the monobasic dibasic ratio and the NH<sub>3</sub> excretion may remain high. After a dose of NaHCO<sub>3</sub> sufficiently great to lower the acidity of the urine and the hourly excretion of the NH<sub>3</sub>, there is an increase in the "acetone bodies," especially hydroxybutyric acid in the latter stages. Much of the alkali ingested must be used to neutralize the retained acids probably at their seat of origin. When general metabolism is at a low level, as in sleep, there is developed a physiol. acidosis somewhat related to the mild diabetic type. J. T. M.

**A new type of human enterolith.** H. S. RAPER. *Proc. Path. Soc.; J. Path. Bact.* 24, 119(1921).—A calculus was obtained from the middle of the jejunum in a case of intestinal obstruction. It consisted of fatty acids, fat, cholesterol, choleic acid, and insoluble food debris. The choleic acid was identified by its m. p., optical activity, and elementary analysis. The preferential deposition of this acid in the small intestine, without appreciable mixt. with the other unconjugated bile acids (cholic and dihydroxycholic), is probably due to the relative insoly. of glycocholic acid which was probably deposited first and decomposed by bacteria producing choleic acid.

JOHN T. MYERS

**The parallel development of the Wassermann reactive body along with the heterophile antibody in the rabbit.** T. TANIGUCHI. *J. Path. Bact.* 24, 122-4(1921).—There is a close similarity in the reaction of the heterophile antibody and Wassermann body with tissue lipoids. There is a parallel development of the two reactions in the sera of rabbits which have been injected with heterophile antigens (guinea pig organs). It is suggested that the development of the Wassermann body in animal sera may be an antibody response similar to the heterophile antibody (C. A. 14, 3458). J. T. M.

**The constitution of the normal hemolysin of ox serum for guinea pig blood, with special reference to filtration experiments and to "conglutinin."** N. YOSHINARI. *J. Path. Bact.* 24, 124-6(1921).—In most instances normal hemolysins possess the same constitution as immune lysis, i. e., a thermostable body with specific combining affinity for red cells along with complement of normal serum. Ox serum filtered through a Berkefeld filter strongly agglutinated guinea pig corpuscles. This conglutinin reaction was independent of the presence of complement and was extremely thermolabile, being destroyed at 45° in 30 minutes.

JOHN T. MYERS

**Diabetes and glucemia.** H. BIERRY AND F. RATHERY. *Compt. rend.* 172, 244-6(1921).—An exptl. study of 45 cases led to the following conclusions: Each diabetic has a glucemic index characteristic of the case. A high figure for this index agrees with

a reserved prognosis. The value of the protein glucemic index, which has not hitherto been considered, is of particular significance in relation to the appearance of coma. The study of the glucemic index gives a means of following the modalities of the diabetic, which is not furnished by an examn. of the urine. L. W. RIGGS

**Nature of the anaphylactic shock.** AUGUSTE LUMIÈRE and HENRI COURTURIER. *Compt. rend.* 172, 294-6(1921); cf. C. A. 15, 1165.—Guinea pigs were sensitized by means of subcutaneous injections of 0.002 cc. horse serum. Twenty days later an intracardiac injection of 0.25 cc. of the same serum produced reactions in 20 to 30 sec. terminating in death near the end of the second min. If 0.5 cc. of 0.265% barytic emulsion is administered by the same route to other animals of the same lot, then, 30 sec. later the 0.25 cc. serum, only slight passing symptoms are observed during the second min. The animals remain crouching but recover without apparent injury. If in 1 min. after the first immunizing injection, a second 10 times as concd. is given the animal supports it perfectly, and at the end of 24 hrs. may receive anaphylactic inoculation, fatal to control animals, without exhibiting serious symptoms. These findings are compared with those of Besredka. L. W. RIGGS

**Role of surface tension in the phenomena of shock.** W. KOPACZAWSKI. *Compt. rend.* 172, 337-9(1921).—K. discusses the work of Lumière and Chevrolier (cf. C. A. 15, 393) and Lumière and Courturier, (cf. C. A. 15, 1165). The density at 15°, viscosity ( $H_2O = 1.0$ ), and surface tension in dynes per cm. were detd. for the substances named in the following list, the figures being those of surface tension: distd.  $H_2O$  73.0, physiol. saline 73.21,  $Na_2S_2O_3$  5% 69.62, normal human serum 66.35, human serum dild. with equal vol. water 69.15, same dild. with equal vol. physiol. saline 67.84, same dild. with equal vol. 5%  $Na_2S_2O_3$  65.63, guinea pig normal serum 68.27, same dild. with equal vol. water 73.42, same dild. with equal vol. physiol. saline 71.28, same dild. with equal vol. 5%  $Na_2S_2O_3$  65.93. These figures support the idea of a relation between flocculation and surface tension; thus, the suppression of the anaphylactic shock by dildn. of the serum injected with its own vol. of 5%  $Na_2S_2O_3$  is attributed to the lowered surface tension. L. W. RIGGS

**Biologic therapy—introduction—general considerations regarding serum and vaccine therapy.** SIMON FLEXNER. *J. Am. Med. Assoc.* 76, 33-4(1921). I. Anti-streptococcus serum and streptococcus vaccines. GEORGE H. WEAVER. *Ibid* 34-5. II. Use of vaccines and serums in gonorrheal urethritis and its complications. JOHN T. GERAGHTY. *Ibid* 35. III. Use of antimeningococcus serum in the treatment of epidemic meningitis. KENNETH D. BLACKFAN. *Ibid* 36-7. IV. Serum treatment of bacillary dysentery. SIMON FLEXNER. *Ibid* 108-9. V. Use of antitoxin in the treatment of diphtheria. WILLIAM H. PARK. *Ibid* 109-10. VI. Serum treatment of acute poliomyelitis. HAROLD L. AMOSS. *Ibid* 110-1. VII. Antipneumococcus serum. RUFUS COLE. *Ibid* 111-2. VIII. Use of tetanus antitoxin in prevention and treatment of tetanus. MATTHIAS NICOLL. *Ibid* 112-3. IX. Acne vaccine therapy. MARTIN F. ENGMAN. *Ibid* 176-7. X. Vaccination against typhoid and paratyphoid fevers. F. F. RUSSELL and H. J. NICHOLS. *Ibid* 177-8. XI. Pneumococcus vaccine. RUSSELL L. CECIL. *Ibid* 178-9. XII. Rabies vaccine. A. M. STIMSON. *Ibid* 241-2. XIII. Pertussis vaccine. WILBURT C. DAVISON. *Ibid* 242-3. XIV. Cholera vaccine. OSCAR TRAGUE. *Ibid* 243. XV. Vaccination against plague. OSCAR TRAGUE. *Ibid* 243-4. XVI. Vaccines in the prevention and treatment of influenza and its sequels. FREDERICK P. GAY. *Ibid* 244-5. XVII. Foreign protein therapy in the acute infections. JOSEPH L. MILLER. *Ibid* 308-10. XVIII. Non-specific protein therapy in arthritis. DAVID M. COWIE. *Ibid* 310-1. XIX. Intravenous protein injections in urology and dermatology. HARRY CULVER. *Ibid* 311-2. XX. The nonspecific reaction. W. F. PETERSEN. *Ibid* 312-3.—These

papers, which make up a symposium on biological therapy, discuss in a general way the status of the specific subjects given.

L. W. RIGGS

**Hemolytic crisis caused by the ingestion of sugar in diabetes.** F. WIDAL, P. ABRAMI AND N. LANCOVESCO. *Presse med.* 29, 121-3(1921).—The ingestion of 20 g. glucose in 200 cc. H<sub>2</sub>O by diabetics causes a drop in the no. of leucocytes. This hemolytic crisis, which becomes evident in about 40 min. and subsides within 1½ hours, occurred in 97% of the diabetics examined, and is absent in other diseases. Lactose, levulose, and sucrose cause a less intense action.

H. A. SHONLE

**Antigens and antibodies.** MAURICE NICOLLE. *J. State Med.* 28, 293-305(1920).—In the first of the Harben Lectures (1920) Nicolle presents his conception of the nature of antigens and antibodies with their mode of action. Cells, animal, vegetable and bacterial, as well as humors, toxins and enzymes function as antigens, stimulating the formation of antibodies, specific in nature and demonstrable by various means. Specificity of action in such obscure substances as enzymes is readily shown by the mode of action of antienzymes such as differentiate the gelatinolytic enzymes of *B. prodigiosus*, *B. pyocyaneus*, *B. proteus* and the cholera vibrio. The antitoxin-producing antigens, toxins, may be classified into three categories: neurotoxins, toxins generating damp slough, and toxins generating dry slough. The first of these act, possibly by hydrolytic action, upon the lipid of nervous tissue; the toxins of damp slough are decoagulating agents, dissolving tissues which have previously been coagulated; those of the dry slough group act in much the same manner but more slowly. All toxins are composed of two distinct fractions, one active and non-antigenic corresponding to simple or relatively simple chem. compds., the other inactive and antigenic representing a colloid substratum. Enzymes are simply the toxins of unorganized matter and act upon substances of more stable character than those against which toxins are directed. Cells and humors act as mosaics of antigens, each type of cell revealing one dominant antigenic group. Each antigen stimulates the formation of but one specific antibody, not as many as there are phenomena observed. Union of the antigen with this specific antibody may be either an association or coagulation process, or a lytic or dissociation process; the latter ensues only in the presence of complement. Agglutination is essentially a coagulation or association phenomenon involving a primary fixation of antibody according to van Bemelen's laws of colloidal adsorption. Sedimentation of the antigen occurs only after this union, and then only in an appropriate electrolyte when the materials are no longer in equilibrium. Precipitin reactions are due to the same processes taking place in connection with albuminous particles. Toxin neutralization *in vitro* is also a process of the same order. The decoagulating or dissociating phenomena—cytolysis, albuminolysis and toxinolysis—are lytic actions involving complement. Antibodies by themselves cause neither coagulating nor decoagulating actions, but by their presence they permit these processes to take place, either by the electrolytes of the medium or by the intervention of complement. Any immune serum possesses both coagulating and decoagulating properties but between them no constant relationship obtains. During immunization the lytic property appears quickly, and reaching a maximum remains stationary or decreases; the coagulating property appears more slowly and increases continuously, the decrease in lytic action being coincident with the progressive increase in coagulating power. This relationship is ascribed to the formation of a single antibody, capable of manifestation in two different ways, either as association or as lysis. Above certain degrees the increase in coagulating property obstructs lytic action. II. *Ibid* 343-53.—N. considers the application of immunological methods to (1) the diagnosis of disease and (2) the detn. of antigenic type. III. *Ibid* 357-67.—The therapeutic application of antigens (vaccines) and antibodies (antitoxic and antibacterial sera) is presented.

G. H. SMITH

**The sources of urobilin.** MARCEL BRULÉ. *J. pharm. chim.* 22, 401-11(1920)  
 —Urobilinuria (*A*) is of neither renal nor entero-hepatic origin (cf. *C. A.* 3, 2180; 4, 783, 1628; 6, 390); urobilin (stercobilin) may occur in the animal intestine even after tying of the bile-duct. *A* is nearly always accompanied by an abnormally high amt. of bilirubin (*B*) in the blood (cf. *C. A.* 2, 670; 3, 668), indicating *biliary retention* in the tissues. Three possible causes for this are given: (a) icterus of hemolytic origin; excessive amts. of *B* are formed in the blood at the expense of hemoglobin. When *B* reaches a certain limit (*seuil d'excretion*), its more diffusive and less toxic reduction product, urobilin, will pass into the urine. As the hepatic function is normal, there is no retention of biliary salts in this case. (b) Obstruction of the bile-ducts, e. g., in lithiasis or certain tumors, involves a rapid and intense retention of bile, resulting even in bilirubinuria. (c) The most frequent cause of *A* is lesion of the hepatic cell, which renders the liver more or less incapable of excreting bile pigments and biliary salts. Thus, testing for *A* becomes a valuable means of qual., although not quant. diagnosis of the early stages of lesions of the liver. *B* doubts the existence of physiol. *A* except perhaps in traces; but transitory *A* has been observed in certain individuals after excess of drink or food or fatigue.

S. WALDBOTT

**Studies of the acid-base equilibrium in disease from the point of view of blood gases.** J. H. MRANS, A. V. BOCK AND M. N. WOODWELL. Mass. Gen. Hospital, Boston. *J. Exp. Med.* 33, 201-22(1921).—CO<sub>2</sub> diagrams have been constructed for the blood of a series of hospital patients as a method of studying disturbances in their acid-base equilibrium. A diabetic with a low level of blood alkali but with a normal blood reaction, a compensated acidosis, showed a rapid return towards normal with no treatment but fasting and increased water and salt intake. A nephritic with a decompensated acidosis and a very low blood alkali was rapidly brought to condition of decompensated alkalosis with a high blood alkali by the therapeutic administration of NaHCO<sub>3</sub>. It is suggested that the therapeutic use of alkali in acidosis is probably only indicated in the decompensated variety and that there it should be controlled carefully and the production of alkalosis avoided.

C. J. WESS

**Studies of chronic intoxications on albino rats. I. Organization of the investigation.** TORALD SOLMALNN, O. H. SCHREYLER AND N. C. WEYZEL. Western Reserve Univ. *J. Pharmacol.* 16, 273-89(1920).—The growth of control rats differs from the "standard growth curve" by a range of -1 to +1.8% per week, with a median difference of +0.13%. Female rats show less variation than male rats. The mean variation from the standard food consumption was 7% (extremes -0.08 and 19%) (0.8 g.). The departures from the standard curves are generally parallel for food and growth, but they are not strictly proportional. II. Alcohols (ethyl, methyl and "wood") and acetone. TORALD SOLLMANN. *Ibid* 291-309.—The continuous consumption by rats of EtOH, in doses of 2.7 to 9.4 cc. per kg. per day, interferes considerably with their growth, and diminishes the consumption of food. Little or no mortality occurs even after periods of months. MeOH and wood alc. and acetone are markedly more toxic than EtOH. MeOH and wood alc., 3.4 cc. per kg. per day as 5% soln., produced very great loss of body wt., greatly diminished consumption of food and drink and caused death within a few weeks. Wood alcohol is rather more toxic than pure MeOH. The same dose in 2.5% soln. produced very few fatalities even after prolonged administration. Their effects on growth and food consumption are more deleterious than those of EtOH in 3 times the dosage. 1.8 cc. acetone per kg. per day as 2.5% soln. is not fatal even after 4 mos. administration. Its effects on growth and food consumption are about the same as 2.5% MeOH. III. Acetic and formic acids. *Ibid* 463-74(1921).—AcOH and HCO<sub>2</sub>H behave approx. quant. alike, when added to the drinking H<sub>2</sub>O of rats, in concns. up to 0.5% and daily doses of 0.36 cc. of absolute acid per kg. body wt., for 2

to 4 mos., this being the sole source of fluids for the animals. Concs. of 0.01 to 0.25% produced no effect on growth, appetite, or consumption of fluid. They are therefore quite harmless. The diuresis described in the literature for formates and acetates must be due to the alk. radical and not the formic radical. With concns. of 0.5%, the appetite and growth but not the fluid consumption are materially, immediately and progressively diminished with both acids. This is evidently due to their acidity, but the expts. do not throw any light as to whether this is due to local action on digestion or whether to some more profound disturbance of the acid-base equil. C. J. WEST

#### H—PHARMACOLOGY

ALFRED N. RICHARDS

A new use for edible oils in surgery. CHAS. BASKERVILLE. *Cotton Oil Press* 4, No. 10, 43-4(1921).—Vegetable oils are sol. in  $\text{Et}_2\text{O}$  and  $\text{CHCl}_3$ , which produce anesthesia when breathed in a gasified form. It is known that the action of these anesthetics is contingent upon their being taken up by the blood. Substances introduced into the intestines may be absorbed into the blood. The difficulty of producing anesthesia for head operations lead J. T. Gwathmey to suggest dissolving  $\text{Et}_2\text{O}$  in oil and administering it as an enema. Since the  $\text{Et}_2\text{O}$  from the mixt. must be liberated slowly enough not to be harmful and yet fast enough to produce anesthesia the rate of evapn. of  $\text{Et}_2\text{O}$  from oil soln. was first studied. Nearly 30,000 successful operations have been performed using the  $\text{Et}_2\text{O}$ -oil colonic anesthesia to produce sleep and in no case were there any disagreeable after-effects. During the war  $\text{Et}_2\text{O}$ -oil solns. were given to many wounded men as a drink prior to dressing serious wounds and proved a great success. H. S. E.

Experimental wound disinfection with trypaflavine. M. FEILER. Frankfurt. *Z. Immunität.* 30, 95-104(1920).—Trypaflavine is suitable for wound disinfection in guinea pigs infected with diphtheria bacilli. The method described is generally applicable to the investigation of substances to be used in wound disinfection.

E. B. FINK

The action of vasomotor substances upon venous pressure in man. I. Adrenaline, papaverine, strychnine. GEORG ROSENOW. Königsberg. *Z. exp. Med.* 10, 333-43 (1920).—The intramuscular injection of adrenaline causes a rise in venous pressure in man. The intravenous injection of papaverine causes a drop in the venous pressure when it follows adrenaline. The action is not const. In normal individuals papaverine has no effect upon the venous pressure. In a case of nephritis with hypertension, papaverine produced a slight drop in venous pressure. Strychnine has no influence upon venous pressure. II. Hypophyseal extract. *Ibid* 344-5.—Following the injection of pituglandol there is a drop in venous pressure. Whether the effect is upon the vessel wall or a combination of vascular and cardiac action remains an open question for the present.

E. B. FINK

The influence of very small doses of nicotine on the human psyche. RICHARD WAHL. Göttingen. *Z. exp. Med.* 10, 352-65(1920).—In non-habituated persons the smallest dose that will begin to produce noticeable effects is 1-2 mg. of the pure base. While heavy smokers tolerate doses up to 8 mg. without showing any marked reaction. Medium-sized doses taken for several days produce greater effects with each successive dose, indicating a cumulative effect of nicotine. Nicotine as such, in any dose, either in non-smokers or heavy smokers, does not possess an action in any way comparable to that of caffeine. The action, if any is produced, is a sense of weariness and loss of energy. The effect of tobacco is not pharmacologic but psychic owing to taste, odor and visual sensations.

E. B. FINK

The pharmacologic action of vuzin and eucuprin. U. G. BYLSMA. Utrecht. *Z. exp. Med.* 11, 257-336(1920).—The pharmacologic action of vuzin dihydrochloride

and eucuprin dihydrochloride as far as studied agrees with that of quinine-HCl. The comparative physical, chem. and biologic properties are given in detail. E. B. FINK

A note on blood pressure during intravenous injections of quinine. U. N. BRAHMACHARI. Calcutta. *Lancet* 1920, II, 1301-2.—Intravenous injection of quinine in concd. soln. is generally followed by a fall in blood pressure and may be followed by the disappearance of the pulse for a few seconds. Less concd. solns. may produce a fall in blood pressure but the action is slower, less marked and may be absent. The slower the injection the less chance of fall in blood pressure taking place. Intravenous injections of quinine in concd. solns. may be followed by muscular twitchings and dyspnea; they should be given slowly, in dil. form together with adrenaline or pituitrin.

E. B. FINK

Comparative studies of the action of digitalis preparations on the heart and vessels of the frog. E. P. PICK AND R. WAGNER. Vienna. *Z. exp. Med.* 12, 28-33(1921).—The preps. studied were strophanthin, digipuratum, cymarín (Bayer), digifolin, digitoxin and digalene. The action of these digitalis preps. falls into 2 groups. The first produces intense vascular constriction and includes cymarín and digitoxin. The second group includes strophanthin, digifolin, verodigen and digalene in which the cardiac action overshadows the vascular effect.

E. B. FINK

A study of drug idiosyncrasy. GUSTAV BAYER. Innsbruck. *Z. exp. Med.* 12, 34-44(1921).—B. reports a case of migraine relieved by antipyrine. When the drug was taken at daily intervals it soon lost its effect. If long intervals elapsed between doses the drug again became effective. There was thus displayed a periodic hypersusceptibility to antipyrine. O. Loew has shown that antipyrine and pyrimidone cause the production of granules ("proteosomes") in certain cells without injuring their vital activity. One may then suppose, applying Liebermann's hypothesis of selective immunity, that an autocatalase is produced, i. e., that these products of the reaction between antipyrine and the cell protoplasm react much more rapidly and strongly with antipyrine than normal protoplasm. The action of these "proteosomes" in the pharmacology of antipyrine and pyrimidone may be compared to that of a crystal upon the salt mols. in a supersatd. salt soln.

E. B. FINK

The distribution of cinchona alkaloids in the blood. ALFRED SCHNABEL. *Biochem. Z.* 112, 112-21(1920).—Using guinea pigs as test animals S. found that the optochin curve in the blood of an intravenously injected subject shows after the preliminary steep fall a secondary marked rise which then gradually falls away to the zero point. This is attributed to a preliminary storage of the alkaloid by the blood cells with a later disengagement.

F. S. HAMMETT

Oligodynamics of silver. III. R. DOERR. *Biochem. Z.* 113, 58-69(1921); cf. *C. A.* 15, 245.—Continuing the previously reported studies D. finds that when Ag which has become inactive is heated to redness the bactericidal and hemolytic properties return if it is allowed to remain in the air for some time. When the metal is kept under melted paraffin the regeneration does not take place and consequently this phenomenon is supposed to be due to the formation of sol. Ag compds. on the surface of the metal owing to the oxidizing influence of the air. It also appears that a unit surface area of the Ag is able to give off to a unit quantity of  $H_2O$  only a certain unit degree of cytotoxic strength, and when this has been given the Ag activity is gone. The repeated addition to a unit amt. of  $H_2O$  of new Ag surfaces containing the sol. cytotoxic compds. increases its activity markedly. This finding is interpreted as showing that the Ag as such is not in colloidal soln. Expts. with typhus, paratyphus-A and paratyphus-B colonies indicate that these organisms in agar when they are placed but a short distance from a bit of Ag can be differentiated from *B. coli* colonies. This difference is accentuated by the

addition of lactose, which is attributed to the differences in acid production from the compd. by the 2 groups. The practical application of this is obvious.

F. S. HAMMETT

**Quantitative studies of the magnesium, calcium and barium sulfate antagonism.** M. KOCHMANN. *Biochem. Z.* 112, 291-309(1920).—Using the frog as the exptl. animal, K. found that  $\text{BaCl}_2$  produces a typical toxic effect of tonic cramps and muscular twitching. The convulsions follow a centrally conditioned course. The lethal dose per kg. frog is about 1 g.  $\text{Na}_2\text{SO}_4$  in doses up to 10 g. in 10% soln. produces no consistent alteration in the animal. This salt has a prophylactic and a curative effect, however, upon the toxicity induced by  $\text{BaCl}_2$ , since many times the lethal dose of the latter can be given without ill effect. The  $\text{Na}_2\text{SO}_4$  is given within 10 to 30 mins. after its injection. This detoxication is attributed to a pptn. of the Ba as  $\text{BaSO}_4$ , since to be effective it must be given in equimolecular amts. and before the toxic substance is fixed in the cells. The antagonism between Mg and Ca is at present inexplicable on a chem. basis.

F. S. HAMMETT

**The influence of  $\text{CO}_2$ , Cl-, and  $\text{PO}_4$ -ions on oxidation processes in the animal body.** RICHARD BING. *Biochem. Z.* 113, 210-30(1921).—This report concerns the results of feeding expts. on dogs in which the effect of various cations was studied by means of the respiratory exchange. Extensive tables are given. The observations lead to the conclusion that when there is a salt deficiency the oxidation processes as well as the energy needs of the body in a condition of absolute rest rise markedly. When the body is salt-poor, the respiratory quotient for 13 to 22 hrs. after a carbohydrate-rich meal is higher than when the food is given with the normal cation mixt. The ingestion of the cation mixt. in the completely fasting condition raises the respiratory quotient not a little; this is interpreted as showing that a part of the carbohydrate still in the body is burned instead of the fat.

F. S. HAMMETT

**The causes of the variations in the reaction of normal human urine.** JULIUS HOLLO. *Biochem. Z.* 113, 246-54(1921).—H. made intravenous injections of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  into various patients and studied the changes induced in the urine reaction thereby. He used the method of titration with 0.2 N NaOH as the basis of his conclusions. The results lead him to the opinion that the healthy kidney answers to the intravenous injection of phosphates with an increased excretion largely of acid salt, even when the alk. salt has been administered and that  $\text{H}_2\text{O}$  drinking increases the output of alk. salt.

F. S. HAMMETT

**Comparative studies on the action of some chloro derivatives of methane, ethane and ethylene on the isolated frog heart.** WERNER KIESSLING. *Biochem. Z.* 114, 292-6(1921).—The pharmacol. action of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{Cl}_2$ ,  $\text{C}_2\text{H}_5\text{Cl}_3$ ,  $\text{C}_2\text{H}_5\text{Cl}_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ ,  $\text{C}_2\text{H}_4\text{Cl}_3$ ,  $\text{C}_2\text{H}_4\text{Cl}_4$ ,  $\text{C}_2\text{H}_2\text{Cl}_2$ ,  $\text{C}_2\text{H}_2\text{Cl}_3$  and  $\text{C}_2\text{H}_2\text{Cl}_4$  on the frog heart was tested. With the exception of  $\text{C}_2\text{H}_4\text{Cl}_2$  and  $\text{C}_2\text{H}_2\text{Cl}_4$  all of the compds. caused ventricular paralysis.

F. S. HAMMETT

**Tremor due to adrenaline.** DIVRY. *Bull. acad. roy. med. Belg.* [5] 1, 27-32 (1921).—A study of adrenaline in the attempt to find drugs with sp. diagnostic effects in the different mental disorders. In all the cases tested 0.5 mg. adrenaline injected subcutaneously induced a tremor, varying with the individual and more or less volitional. The response seemed somewhat less in the case of general paralytics and somewhat greater in the case of alcoholics.

M. HEIDELBERGER

**Behavior of alcohol in the human body.** W. SCHWEISHERMER. *Munich. Schweiz. Chem. Ztg.* 1920, 524-4. —Ingested alc. is absorbed from the stomach and intestine, and may attain a concn. of 1 or 2 parts per 1000 in the blood; a small portion is excreted unchanged in the urine and expired air; the major portion is burned in the body, possibly in the liver. With an increase in the alc. content of the blood, the symptoms of drunk-



eness become more pronounced. The same amt. of alc. is more rapidly absorbed and burned, and produces a lower concn. of alc. in the blood in the case of a chronic drinker than in the case of an abstainer; a moderate drinker falls into an intermediate position. However, when the body cells are used regularly to burn alc., they then function less readily in overcoming infection, should the body be attacked by a disease of this type. A person who has used alc. for a decade or more may lose the acquired ability to burn alc. rapidly; this loss is due to injuries to the vital organs. JOSEPH S. HEFURN

The local anesthetic properties of benzoylcarbinol. A. M. HJORT AND C. E. KAUFMANN. Yale Univ. School of Med. *Proc. Soc. Exp. Biol. Med.* 17, 79-80(1920).—Benzoylcarbinol possesses local anesthetic properties which in general are superior to those of benzyl alc.,  $\alpha$ -methylbenzyl alc. and phenethyl alc. Benzoylcarbinol is less irritant to the body tissues than these compds. and is the most stable of the series. Its soly. in  $H_2O$  is sufficient to make it a practicable local anesthetic. V. C. MYERS

Poisoning by nitro-halogen derivatives of methane. ANDRÉ MAYER, PLANTROU, AND FRED VLES. *Compt. rend.* 171, 1396-7(1920).—Upon inhalation these derivs. produce an edema from which, at the moment of death, the liquid may equal 58% of the total wt. of the lungs. Bromopicrin and dichlorodinitromethane have but  $1/4$  to  $1/10$  the activity of chloropicrin. When injected intraperitoneally, death is probably caused by the formation of methemoglobin. In this action  $C(NO_2)_4$  and  $Cl_3C(NO_2)_2$  gave 80 to 100 and 58 to 100 as the respective ratios of methemoglobin to hemoglobin.  $ClC(NO_2)_2$  gave a ratio of less than 2 to 100. The measurements were made spectroscopically. L. W. RIGGS

Case of borax poisoning. CARYL POTTER. *J. Am. Med. Assoc.* 76, 378(1921).—A man aged 66 took perhaps 60 g. of borax by mistake, and within 15 min. was seized with violent cramps, vomiting and a sensation of strangling. Death occurred in 3 hrs. At necropsy 42 g. of borax were found in the stomach. Greater care should be used in labelling and handling household borax as it is popularly supposed to be non-poisonous. L. W. RIGGS

Administration of carbon dioxide after anesthesia and operation. The acid-base regulatory mechanism. STANLEY P. REIMANN, GEORGE H. BLOOM AND HOBART A. REIMANN. *J. Am. Med. Assoc.* 76, 437-40(1921).—The technic and findings are reported for 8 persons and 4 dogs. In view of the expts. and results reported, and in consideration of the therapeutic and theoretical bases of  $CO_2$ , contrasted with the administration of an alkali, the use of  $NaHCO_3$  in a practical way is indicated.  $NaHCO_3$  should be given to selected surgical patients. The use of  $CO_2$  by inhalation is contraindicated. L. W. RIGGS

Zinc chloride poisoning—report of outbreak among workers in a wood preserving industry. CAREY P. MCCORD AND C. H. KILKER. *J. Am. Med. Assoc.* 76, 442-3(1921).—Workmen who handled railway ties which had been treated with tar and  $ZnCl_2$  soln. suffered from lesions on the hands and fingers which generally developed at the site of an abrasion of the skin. The  $ZnCl_2$  "burns" were different in appearance from the eruptions caused by tar. They were treated effectively by removing the escharotic tissue and filling the crater with  $NaHCO_3$  alone or mixed with petrolatum. The burns were prevented by wearing "flexible lined canvas gauntlets," which were impervious to all fractions of the treating fluid, and were comfortable, durable and inexpensive. L. W. RIGGS

Comparison of rectal with colon injections of epinephrine with reference to pressor effects and to glucosuria. HENRY G. BARBOUR AND FREDERICK H. RAPOPORT. *J. Am. Med. Assoc.* 76, 492-4(1921).—With rabbits the av. amt. of dextrose, max. amt. of dextrose, and av. amt. of urine in 24 hrs. after colon injection of 0.5 g. of epinephrine per kg. were 0.158 g., 0.208 g., and 142.5 cc. resp. By rectal injection the corresponding

figures were 0.088 g., 0.121 g., and 120 cc. Injection into the rectum caused a greater rise in blood pressure than injection into the colon.

I. W. RIGGS

The action of adrenaline on the heart. R. LUTENBACHER. *Presse med.* 29, 145-6 (1921).—Adrenaline, with total and partial heart block, independently accelerates the beat of the auricles and ventricles, when injected intravenously. After the accelerating phase, the beat may be retarded for several days.

H. A. SHONLE

The new pharmacology. THOMAS YULE. *Pharm. J.* 106, 110-2 (1921).—An exposition of the trend towards simple as against polypharmacy, based on the works of T. Sollmann and A. R. Cushny.

S. WALDBOTT

Testing Swedish *Scopolia carniolica* (ENGFELDT, LILJESTRAND) 17. New benzyl esters possessing an antispasmodic action (SHONLE, ROW) 10.

### I—ZOOLOGY

The reasons for the variation in the effects of formaldehyde as a poison for house-flies. L. LLOYD. *J. Ent. Research* 11, 47-63 (1920).—HCHO containing  $(\text{CH}_3)_3\text{N}$ ,  $\text{CH}_3\text{NH}_2$ , and  $\text{HCOOH}$  was found to be repellent to the house fly (*Musca domestica*) when used as a stomach poison. Impurities such as trioxymethylene, methylal, MeOH, EtOH and acetone were found to be neutral or of little importance in their influence upon the attractiveness of poisoned baits or  $\text{H}_2\text{O}$  containing HCHO. Samples of HCHO containing acid were rendered suitable as fly poisons by the addition of a weak alkali such as  $\text{Ca}(\text{OH})_2$ .  $\text{NH}_4\text{OH}$  is non-suitable. The effectiveness of baits containing HCHO is greatest under conditions of low atm. humidity. Exptl. data are given relative to the deterrent effect of HCHO and toxicity and a comparison is made with other poisons in which it is shown that HCHO is safer and more economical than Na arsenite and the equal of NaF in toxicity. The formula recommended for poisoning flies is as follows: HCHO (40%) 5-6%, clear lime water 50%, sucrose 2.5%,  $\text{H}_2\text{O}$  to make 100%.

CHAS. H. RICHARDSON

R. A. GORTNER

Studies of some extractives of *Cryptobranchus japonicus*. A contribution to the subject of creatine formation in the animal body. ILSE REUTER. *Z. Biol.* 72, 129-40 (1920).—R. was able to demonstrate the presence of creatine, methylguanidine and sarco-lactic acid in exts. from the tissues of *Cryptobranchus japonicus*. No arginine could be found but in its place there was a substance yielding a well crystd. Au salt that differed sharply from tetramethylarginine aurate. He considers that creatine metabolism in cold-blooded animals follows the same laws as in warm-blooded animals.

F. S. H.

Physiological studies on Planaria. IV. Oxygen consumption during starvation. LEBBIE H. HYMAN. Univ. Chicago. *Am. J. Physiol.* 53, 399-420 (1920); cf. *C. A.* 14, 2222.—Further expts. with *Planaria agilis* and *Planaria maculata* support H.'s earlier work (*C. A.* 14, 3245). Contrary to the results of Allen (*C. A.* 13, 3245) in both of these species within the time limit specified in his paper, the rate of O consumption is increased in the later periods of starvation. The general conception maintained by Child that the metabolism of organisms is increased in starvation and that starvation is therefore a means of rejuvenescence is supported.

J. F. LYMAN

Changes in acid and alkali tolerance with age in planarians, with a note on catalase content. J. W. MACARTHUR. Univ. Chicago and Univ. Toronto. *Am. J. Physiol.* 54, 138-46 (1920).—Smaller, physiol. younger, individuals of *Planaria dorotocephala* are on the av. tolerant of a slightly wider range of  $\text{H}^+$  concn. (from  $p_{\text{H}}$  4.7 to 9.3) than are larger, physiol. older individuals. The young possess a greater power of neutrality regulation than do the old. In concns. which kill within a few hrs. susceptibility is

reversed in relation to water, the young being more susceptible than the old. Young planarians have about double the cathecol content of old planarians per g. of tissue.

J. P. LYMAN

**Fertilization—reaction in Echinarachulus parma.** IV. Further analysis of the nature of butyric acid activation. R. E. JUSZ. *Biol. Bull. Marine Biol. Lab.* 39, 280-304(1920).—There appears "a clear cut difference between the butyric acid-treated egg with a membrane and the overexposed egg with a jelly-like cortex. The overexposed egg is an egg in the initial stages of cytolytic; its jelly-like cortex marks the beginning of cytolytic." Short exposures (10 to 20 sec.) to 2 cc. 0.1 *N* butyric acid in 50 cc. sea water appear beneficial in conserving fertilization power. Longer exposures, e. g. 90 secs., are decidedly harmful. The activation of the egg, whether produced through sperm or through butyric acid, renders the egg incapable of insemination. The underlying process of membrane formation is a secretion or liquefaction of the cortex. The activated egg is one that has lost its fertilizin. The overexposed egg is capable of insemination but does not form membranes when inseminated. The overexposed egg is still capable of fertilization and secretes fertilizin. It is a cytolytic egg. Activation is not a cytolytic. The views of Loeb, that activation is a cytolytic, are discussed at length.

L. W. RIGGS

**Physical effects of anesthetics upon living protoplasm.** L. V. HALLBURN. *Biol. Bull. Marine Biol. Lab.* 39, 307-15(1920).—There are 2 types of anesthesia in the sea urchin egg. In one the viscosity of the cytoplasm is decreased, in the other it is increased. When the viscosity is decreased sufficiently, the mitotic spindle is always prevented from forming. Anesthetics like cyanide and hypertonic solutions allow the formation of spindles. In both cases the protoplasmic viscosity is held fixed.

L. W. RIGGS

**Studies of fertilization. VIII. Measure of specificity in fertilization between two associated species of the sea-urchin genus Strongylocentrotus.** FRANK R. LILLIE. Univ. Chicago. *Biol. Bull. Marine Biol. Lab.* 40, 1-22(1921).—Specificity in fertilization and in sperm agglutination appear to be related phenomena. "The change in the spermatozoon produced by the fertilizin of its own species must in some way be connected with the relative ease with which the spermatozoon fertilized the egg of its own species. The fertilizin theory gives a reasonable view of this relationship. The variable percentages of cross-fertilization would show that a degree of reaction which would not suffice for agglutination of the spermatozoa may yet be sufficient under favorable circumstances for activation of fertilizin." IX. Superposition of fertilization of parthenogenesis in *Strongylocentrotus purpuratus*. *Ibid.* 23-31(1921).—Conclusion: "The membrane reaction after butyric acid treatment is the same as after insemination; this is shown by similarity of the membranes formed in the two cases, and by the fact that the rate of formation is the same. The result of rendering the egg insusceptible to spermatozoa shows a possible slight difference only, and this receives an obvious explanation on the assumption that there is a variable tendency towards incompleteness of reaction after butyric acid which in rare cases leaves some of the reacting substance of the egg (fertilizin) free for sperm action."

L. W. RIGGS

**Biologic semipermeability of the exterior walls of Sipunculideae.** C. DICKINSON. *Compt. rend.* 172, 238-41(1921).—The interior liquids of marine invertebrates are isotonic with the surrounding sea  $H_2O$ . Expts. were made by weighing the animals, immersing them in a hypotonic liquid consisting of 100 cc.  $H_2O$  and 900 cc. sea  $H_2O$ , and in a hypertonic liquid obtained by dissolving 3.5 g. NaCl in one liter sea  $H_2O$  for 24 hrs. and again weighing, after which the animals were restored to sea  $H_2O$  and weighed after 1 to 3 hrs. The results showed that the exterior wall of *Phascolosoma*

surface and of *S. typhimurium* is biologically semipermeable, which means that  $\text{H}_2\text{O}$ ,  $\text{Cl}_2$ , and  $\text{O}_2$  pass with a velocity incomparably greater than that of milk.

L. W. RIGGS

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

The detection of milk altered by secretion disturbances. G. KOESTLER. *Mitt. Lebensmittel Hyg.* 11, 184-86 (1920).—Investigations described show that the usual tests are of no value for control work in detecting milk altered by secretion disturbances. Bacteriological and enzyme tests are useless unless applied on the milk direct from the udder. The usual detn. of the cell content (cell count) cannot be used. The acid value, and other similar tests (rennet reaction, coagulation with alc., decoloration of methylene-blue soln., and alizarol pptn.), as well as the detn. of serum-sol. N, are not applicable. Slightest pathological disturbances affect the milk, increasing the serum-sol. N, Cl, and Na, and decreasing the lactose, K, and  $\text{P}_2\text{O}_5$ . A relative rise in Cl and a decrease in lactose content takes place with the slightest or greatest secretion disturbance. A "chlorine-sugar" no., 100 (chlorine/lactose), which increases with the intensity of the disturbance can be used to detect altered milk. The values of the no. were found to be 0.49 to 15 for normal and pathological milk, resp. The latter was to all outward appearance a normal milk. Definite values are not given to distinguish normal from slightly altered milk. The ratio of Cl to  $\text{P}_2\text{O}_5$  in the ash may also serve to detect altered milk. The altered milk studied showed a normal lowering of the freezing point and in cases where the general analytical results (deficient fat-free solids and low N of serum) indicate watering the freezing-point detn. is a valuable check. The stall test will aid in detg. whether a milk is mixed with pathological udder secretions. Milk from each udder is taken separately and compared by the above method with the suspected milk.

H. A. LEPPER

Sanitary control in food inspection. J. H. KNAPP. *Chem. Age* (New York) 28, 423-4 (1920).—The system of control in food inspection as carried on in the city of Cleveland, O., is described.

H. A. LEPPER

What chemistry can do in the food industry. R. S. HILTNER. *Chem. Met. Eng.* 24, 242-4 (1921).—A brief discussion of work to be done and of the good results derived from the application of chemistry to obtain more, better and cheaper food.

E. J. C.

Emergency ration of the American army. F. ROTHÉA. *Bull. sci. pharmacol.* 28, 106-10 (1921).—This study of the chem. compn. and fuel value of the emergency ration of the Am. army deserves attention and confirmation, inasmuch as the analyses obtained by R. demonstrate that the material is far from sufficient to supply adequate nourishment for an active man for the stated period of 24 hrs. The chocolate cakes supplied contain  $\text{H}_2\text{O}$  1.84, ash 1.95, nitrogenous matter 7.28, fats 25.63, sucrose 46.92 non-nitrogenous extractives (starch, etc.) 16.40%. The conclusion from the analysis is that the cakes are made of approx. equal parts of pure cocoa and sucrose. The meat biscuit contains  $\text{H}_2\text{O}$  9.78, ash 3.51, nitrogenous materials 53.43, fats 2.58, amylaceous matter 47.09, cellulose debris 1.61%. R. concludes that the biscuits are a mixt. of whole flour and meat powder, the latter constituent having been defatted. The total cals. as calcd. on the basis of digestibility are but 1.239, hardly an adequate ration.

F. S. HAMMETT

Detection of manurial pollution in milk by the anaerobic spore test. JOHN WEINZ. *Am. J. Public Health* 11, 149-52 (1921).—In the test for anaerobic spores 0.5-1 cc. of melted paraffin is placed in a 15 mm. test tube, which is plugged with cotton and

sterilized by dry or moist heat. With a sterile pipet 5 cc. of the milk under test are placed in each of 5 tubes containing paraffin. These tubes are then placed in an Arnold sterilizer and heated to 80° for 10 to 15 min. This melts the paraffin which rises to the surface, where upon cooling it hardens and forms the anaerobic seal. The heat also expels O absorbed by the milk, thus rendering anaerobiosis more complete. All vegetative bacteria in the milk are killed by the heat, only the spore forms remaining. Tubes are then incubated for 3 days at 37°. If anaerobes are present gas will be formed which lifts the paraffin plugs in the tube. Two positives out of 5 tubes condemns the milk as showing excessive pollution. Results tend to show that the test will reveal 76% positives. This result is probably too low, owing to caramelization of the lactose during autoclaving. When lactose was added the sensitiveness was 95.8%. This study seems to show the anaerobic spore test far superior to total count or visible dirt tests, and it apparently equals the *B. coli* test for this purpose. N. VAN PATTEN

The baking powder question. J. PRITZKER. Basel, Schweiz. *Apoth. Ztg.* 58: 526-30(1920); cf. C. A. 14, 2385.—A review of recent articles by A. Fornet (C. A. 14, 1860, 2519), K. Brauer (C. A. 14, 1861, 3285) and Grünhut (C. A. 14, 1887, 2086). P. upholds the chem. standards as against baking tests only; still, the German standard of 2.35 to 2.85 of active CO<sub>2</sub> per 0.5 kg. of flour is too high; 1.5 g. should be sufficient; 1.65 g. gave a good baking test (A. F.). Detn. of excess of NaHCO<sub>3</sub> is essential. Results by B.'s method are unreliable, as G. has shown that NaHCO<sub>3</sub> on evapn. tends to form a sesquicarbonate, Na<sub>2</sub>H<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>; hence any method of detn. of NaHCO<sub>3</sub> from CO<sub>2</sub> evolved must fail. G.'s recent method is recommended. S. WALDBÖTT

Flour milling and the cereal chemist. R. WALLACE MITCHELL. *Chem. Age* (N. Y.) 29, 85-9(1921).—Characteristics of wheat and the duties of the cereal chemist are discussed. E. H.

Wheat flour. I. Electric conductivity of water extracts. C. H. BAILEY and F. A. COLLATZ. *J. Ind. Eng. Chem.* 13, 319-21(1921).—See C. A. 14, 3729. E. H.

Detection of methyl anthranilate in fruit juices. FREDERICK B. POWER. *J. Am. Chem. Soc.* 43, 377-81(1921).—The following practical and trustworthy method for the detection of *o*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me (A) in grape juice has been developed; about 500 cc. is distd. with steam, 200 cc. distillate collected, extd. 3 times with 10 cc. CHCl<sub>3</sub>, filtered through a dry paper, cautiously evapd. on the H<sub>2</sub>O bath in a current of air, immediately treated with 2 cc. of 10% H<sub>2</sub>SO<sub>4</sub>, cooled, treated with 1 drop of 50% NaNO<sub>2</sub> and a few crystals of urea and added to a mixt. of 1 cc. of 0.5%  $\beta$ -naphthol, 1 cc. of 10% NaOH and 1 cc. of 10% Na<sub>2</sub>CO<sub>3</sub>.H<sub>2</sub>O; if not less than 0.0001 g. A is present a yellowish red ppt. is formed. In the presence of not less than 0.001 g. A, 1 drop of PhNMe<sub>2</sub> and then a slight excess of 10% NaOH added to the 2 cc. of diazotized soln. produces a yellowish color changing to red on acidifying with dil. H<sub>2</sub>SO<sub>4</sub>. C. A. ROULLER

Influence of electrolytes on the amount of soluble extract in corn flour. MICHELIS and HENNERS. *Bull. acad. roy. méd. Belg.* [5] 1, 71-82(1921).—Cf. C. A. 14, 3286.—Twenty g. in 200 cc. H<sub>2</sub>O satd. with CHCl<sub>3</sub> and containing increasing amts. of the salt in question were shaken from time to time during 7-12 hrs., filtered, an aliquot of 50 cc. taken, and this evapd. dry at 100°, deducting the content of the salt used. As in the previous studies, the alums had the max. depressing effect, culminating in Fe alum, this being attributed to the known power of trivalent ions to ppt. colloids. CuSO<sub>4</sub> also diminished the ext. greatly, even in low concns., thus differing from its action on wheat flour. K<sub>2</sub>CrO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> reduced the ext. NiSO<sub>4</sub>, MnSO<sub>4</sub>, MgSO<sub>4</sub>, BaCl<sub>2</sub>, and H<sub>2</sub>Ac had little effect, ZnSO<sub>4</sub> showed a reduction above 0.25%, while KNO<sub>3</sub> and K<sub>2</sub>Fe(CN)<sub>6</sub> caused slight increases. M. HEMMELHANS

**Prunose (Damm.) 28.** Physiological value and toxicity of cottonseed and some of its products (Macy, Menden) 11E.

**Reichwald, Egon:** Probleme und Aufgaben der Nahrungsmittel-Chemie. Dresden and Leipzig: Verlag von Theodor Steinkopff. 99 pp. \$75.

**Food mixture prepared for baking.** H. M. BLINN. U. S. 1,370,272, Mar. 1. All ingredients essential to making cake or biscuit are incorporated in dry form, including shortening material such as a hydrogenated oil or fat which is highly resistant to rancidifying influences.

**Food from fish.** S. SATOW. U. S. 1,370,049, Mar. 1. Cooked residue from fish oil manuf. is crushed or ground to a paste, dried *in vacuo* at a temp. below 10°, reduced to a powder, treated with a proteolytic enzyme such as pepsin to solubilize the albumin content of the mass, extd. with H<sub>2</sub>O and the ext. thus obtained is dried and powdered for use as a food.

**Calcium peroxide in bread making.** C. J. PATTERSON and R. W. MITCHELL. U. S. 1,370,354, Mar. 1. CaO<sub>2</sub> up to about 0.007% the wt. of the flour is incorporated in bread dough to increase its capacity for moisture.

**Reagent for the determination of fat in milk.** T. OSHIDA. Japan 36,282, Apr. 28, 1920. The reagent is prepd. by mixing 3.5 cc. pure alc., 5.6 cc. H<sub>2</sub>O, 3.5 cc. amyl alc., 1.0 cc. glycerol, 0.005 g. methylene blue, and 0.0025 g. sudan. Eleven cc. of the reagent are mixed with 10 cc. milk at 15°, put in the Gerber lactobutyrrometer, shaken and mixed, warmed for 5-6 min. at 65-70°, centrifuged for 3 min. and read at 40°. The border is distinct, as the upper fat layer is red and lower one blue.

**Confectionery.** T. N. RHADING. Brit. 155,724, Feb. 13, 1920. Kernels of cheap uncolored nuts, or cereals such as maize, are colored by immersion in a vegetable dye, dried in a hot chamber, and used for the decoration of confections, biscuits, etc., as a substitute for more expensive naturally colored kernels. Rectified spirits of wine, sweet nut oil, or hot H<sub>2</sub>O may be used to dissolve the dye, and the dye may be allowed to penetrate into the kernels to any desired extent.

**Apparatus for carbonating beverages.** C. N. JACOBY. U. S. 1,370,213, Mar. 1.

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

**The chemical industry and trade of Switzerland.** O. P. HOPKINS. *J. Ind. Eng. Chem.* 13, 285-92 (1921). E. J. C.

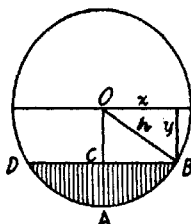
**The storing of volatile liquids.** J. MARTIN. *Mat. grasses* 12, 5634-6 (1920).—A general discussion. E. SCHERUBEL.

**The recovery of volatile solvents.** PAUL RAZOUS. *L'industrie chimique* 6, 195-7 (1919).—The process of Georges Claude is employed for the recovery of alcohol and ether when diluted with a large volume of air. There may be 5-25 g. of the liquid per cu. m. of air. The mixt. is compressed under 4 atm. in a water cooler, expanded and the temperature gradually lowered in tubular temperature changer. This method and that of Clément and Riviere are described in considerable detail, with diagrams. They are mostly used for alcohol-ether solvents of Chardonnnet silk works, smokeless powder factories, celluloid, etc. The Brégeat app. is very completely described and explained. It is very extensively employed and has many advantages. It gives easy absorption of volatile solvents, even when dild. in large vols. of air or as low as 2 g. per cu. m. Some advantages are the use of cheap solvents, especially cresol; easy regeneration of volatile solvents, which can be reemployed. The action is either con-

tinuous or intermittent. *Ibid* 229-31.—The usual methods are reviewed. Diagrams of recovery in open circuit, in closed circuit, and in shunted circuit are given and described. A process of recovery by compression and expansion and a process by utilizing a relatively fixed liquid successively absorbing the solvent and disengaging it by heat are described. By the recovery of solvents these liquids may be regarded as tools and machines constantly in service in any given factory.

L. G. SMITH

New simplified formula for calculating the contents of horizontal cylindrical vessels. FR. BÜRK. Mannheim. *Chem. App.* 7, 177-8(1920).—The formula is  $F = r^2 \arcsine(x/r) - xy$ . In the sketch, let the vessel be filled to the level  $DCB$ ; then  $F$  = the



area of the cross-section  $ABCD$ ,  $r$  = radius of the vessel,  $x$  = half the chord  $BD$ , and  $y$  = the ordinate. By "arcsine  $x/r$ " is meant the arc on a circle of radius = 1 whose sine is equal to  $x/r$ . Example: If diam. of vessel is 3000 mm. and it is filled to a depth of 700 mm., what is the contents per 1 m. length?  $r = 1500$ ;  $y = 1500 - 700 = 800$ ;  $x = \sqrt{1500^2 - 800^2} = 1268.86$ . Therefore,  $F = 1500^2 \times \arcsine(1268.86/1500) - 1268.86 \times 800$ .  $1268.86/1500 = 0.8458$  = an angle of  $57^\circ 45'$ . Now, an angle of  $360^\circ$  corresponds to a circumference of  $2\pi$  on a circle of  $r = 1$ ,  $90^\circ = \pi/2$ ,  $1^\circ = \pi/2 \times 90$ ,  $1' = \pi/2 \times 90 \times 60 = \pi/10800$ . Therefore,  $57^\circ 45'$ , or  $3465' = 3465 \times$

$\pi/10800 = 1.008$ , which is the "arcsine  $1268.86/1500$ ," and which, by substituting, gives a content of 1254.3 l. per 1 m. length.

J. H. MOORE

The colloidal mill and its use in the large chemical industries. BERTHOLD BLOCK. Charlottenburg. *Z. angew. Chem.* 34, Aufsatzteil 25-30(1921).—The 1st part of the paper is a review of previous results in the prepn. of colloidal substances and a mathematical discussion of the power required. It is followed by an incomplete description, with 3 cuts, of H. Plauson's colloidal mill which operates on the principle of suspending the material to be pulverized in some medium, as  $H_2O$ , which is subjected to a beating process by means of arms on a rapidly revolving drum inside an outer casing. It is said that because of the incompressibility of the medium the particles receive the full force of the blow delivered by the arms, that with substances which will absorb the medium (e. g., cellulose in  $H_2O$ ) there is an explosive action tending to pulverize the substance, that the heat liberated, the frictional electricity generated, the addition of suitable chemicals to the medium and the proper adjustment of the quantity of the medium to that of the substance all assist in reducing the material to the colloidal condition. Diagrams of plants for making colloidal cellulose and for working up oil-bearing shales are given, and also 2 cuts of app. for measuring the progress of the pulverization.

J. H. MOORE

Colfax—a superpower plant at the mouth of a coal mine. ANON. *Elec. World* 77, 753-60(1921), 7 illus.—A detailed account.

C. G. F.

Power-heating operations. O. BUCHSTEIN. *Chem. App.* 8, 29-32, 44-5(1921), 6 cuts.—A discussion of the economies effected by using the exhaust steam from power plants for heating purposes, with tables and cuts showing the heat distribution in power plants, the heat production, gradient, and steam used per h.p.-hr. with differing steam conditions, the heat consumption of various types of engines per h.p.-hr., the heat distribution when the heating and power plants are sepd. and when combined, and a chart comparing the economy of the 2 systems with engines up to 300 h.p., using steam at 13 atms. absolute and 2 atms. back-pressure.

J. H. MOORE

Lubrication of air compressors. H. V. CONRAD. *Glass Ind.* 1, 41-3(1921).—Specifications are given for oils to reduce friction to a minimum and eliminate carboniza-

tion as far as possible. Tables are given showing the quantity of oil which should be used in air and steam cylinders. Asphalt-base oils, not compounded with fixed oils, are preferred, because the C deposit is fluffy.

EUGENE C. BIGHAM

**Graphite lubricants.** W. R. G. ATKINS. *J. Soc. Autom. Eng.* 3, 374(1921).—A graphite film in a bearing reduces the solid friction of metal to metal and provides a skin which is removed from the oil, this skin being worn away instead of the metal. After graphite has been in use in an engine for some time, the amt. in the oil, always a small quantity, can be further reduced, for once the graphite surface is formed, a very small quantity suffices to maintain it. It is suggested that an explanation of the reduction in the consumption of lubricating oil when used in conjunction with graphite is that by reducing the friction and the eddy currents in the oil due to surface irregularities, the temp. of the oil film is on an av. reduced, and its viscosity being on that account greater, the rate of flow is diminished.

R. L. SIBLEY

FOA, Z. MICHELE: Saggi chimici elementari sulla genuinità delle principali merci ad uso degli studenti di mercologia degli Istituti Tecnici, Commerciali e Superiori di Commercio, dei Commercianti e degli industriali. Torino and Milan: G. B. Paravia e C. 308 pp. L. 8. For review see *Boll. chim. farm.* 59, 405(1920).

**Distillation.** W. K. LEWIS and W. GREEN. *Brit.* 155,511, Jan. 31, 1919. A volatile solvent or other liquid is distd. from its soln. in a heavy oil, etc., by passage through a series of superposed separately heated and perforated pans so arranged in a casing that the resulting vapors flow in countercurrent to the descending liquid. The pans are so spaced that a uniform vacuum is maintained through the casing. The heating is effected by steam coils. The vapors are led to a condenser for the sepn. of any heavy oil that may be volatilized and are then passed through a heater and mixed with dry air or other gas, admitted by a pipe, before admission to a steam-jacketed vacuum pump. The pump discharges to a condenser, a rough vacuum pump and condenser. The app. is specially suitable for treating the soln. obtained in recovering a solvent as described in 152,374 (*C. A.* 15, 716).

**Purifying liquids.** J. N. A. SAUER. *Brit.* 155,611, June 20, 1919. Saccharine and other liquids are purified by subjecting them to the action of decolorizing C or similar substance, the amt. of C being in excess of what is required for complete purification. The same batch of material is then used without regeneration to purify further quantities of the liquid. It is stated in the specification that the following substances may be used in a similar manner: kieselguhr, fuller's earth, phosphates, carbonates, sulfates, and sulfites of CaO, etc. Cf. 7119, 1902, and 8627, 1912 (*C. A.* 7, 3224).

**Cooling and solidifying emulsions, etc.** H. J. BIGUM. *Brit.* 155,755, Dec. 21, 1920. Relates to rotary internally cooled drums upon which emulsions, etc., are spread in films and removed by a scraper when solidified, the drums being of the type provided with annular or longitudinal strengthening-ribs. A suitable construction is specified.

**Effecting chemical reactions.** M. BRUTZKUS. *Brit.* 155,776, Dec. 22, 1920. Chem. reactions are carried out in the interior of a compressor under such conditions that the reacting substances are first brought to a suitable temp. and pressure either by compression, expansion or other means, and are then brought to reaction while maintaining the temp. and pressure substantially const. This latter condition is attained by starting the reaction at a selected point of the cycle, that is at a point on the inward or outward stroke of the piston; by the gradual introduction of one or more of the reacting substances; and by the addition or abstraction of heat while the reac-



tion is taking place. In general, the selection will depend on whether the reaction is endothermic or exothermic, and whether it is accompanied by an increase or decrease in the number of mols. or whether the number of mols. remains the same. For the addition or abstraction of heat, heating or cooling liquids may be directly injected into the cylinder or may be circulated through its jacket or through spiral tubes passing through the end compression space; or flame arcs or other elec. heating-means may be employed. For catalytic reactions, the necessary catalysts may be placed in the end compression space or may be attached to the piston, and they may be heated by the elec. heating-means. Other reactions may be effected by elec. sparks or discharges, or ultra-violet light. The reaction products under pressure may be allowed to escape, or the energy in them may be recovered by allowing them to expand in the cylinder. The following are processes for which the invention is applicable:  $CH_3CHO$  from  $C_2H_2$  and  $H_2O$  vapor—these are brought to reaction during the compression stroke, and the temp. and pressure is maintained const. by injecting  $H_2O$ ;  $HCHO$ , by a similar process in which air is added;  $HOAc$ , by a similar process but substituting  $H_2O_2$  for  $H_2O$  vapor;  $HCN$ , by the combination of  $C_2H_2$  and  $N$ , the reaction being carried out during the compression stroke by means of "induction sparks," while strongly cooling by the addition of cooled  $N$ ; *pyridine* and *pyrrole*, by a similar process using  $C_2H_2$  and  $NH_3$ , except that to start the reaction flowing surfaces are used in the place of "induction sparks;"  $HCHO$ , by the combination of  $H$  with  $CO$  and  $CO_2$  under pressure and in the presence of heated  $Pt$  wires, increase in temp. and pressure being obviated by injecting  $H_2O$ ;  $NaOAc$ , by injecting into compressed  $CO$  "liquid caustic soda" containing sufficient  $H_2O$  to obviate an increase of temp.;  $HOAc$ , by combining steam and  $CO$  at very high temps.; the *synthetic production of  $NH_3$* —in this case the reaction is started at about the middle of the compression stroke and thereafter increase of temp. and pressure is prevented by the injection in the liquid state of the reaction gases, singly or mixed, or of  $H_2O$ , and the compressor may be operated according to a 4-stroke or 2-stroke cycle and may be in the form of a Diesel motor, and the  $NH_3$  may be removed without loss of the residual gases by injecting  $H_2O$  into the cylinder and allowing only the resulting soln. to escape, and the formation of the  $NH_3$  may be assisted by "induction sparks" or silent elec. discharges; the *polymerization of  $C_2H_2$* , by compressing the latter in the presence of suitable protective gases or vapors, and in this condition subjecting it to the action of suitable catalysts or other physical agencies; the *cracking of hydrocarbons*—in this case the reaction is carried out during the expansion stroke; the *hydrogenation of fatty acids*,  $H$  being first compressed and the fatty acid sprayed in while the  $H$  is being compressed still further; *sapons*.—these are effected during the compression or expansion strokes according as the reaction is endothermic or exothermic; the *production of ozone*— $O$  is compressed and during the remaining part of the compression stroke is subjected to "induction sparks," silent discharges, or ultra-violet light, the gases being released at the end of the compression stroke in order to prevent decompn. of the ozone; the ozone so obtained, may be employed *in situ* for effecting the oxidation of methane, illuminating gas,  $C_2H_6$ , alc., etc., to alc.,  $CH_3CHO$ , acids, etc., of isoeugenol to vanillin, and of steam to  $H_2O_2$ ; *N oxide*, by exposing aft rich in  $O$  during the compression stroke to ultra-violet light or elec. arcs, and at the end of the stroke exhausting the gases through a suitably cooled valve, to prevent decompn. of the  $N$  oxide; *O from air*, by absorption in  $BaO$ ,  $CuCl_2$ , etc.—the cylinder is filled with  $O$  under a pressure such that at the end of the compression stroke its temp. is sufficient to cause the  $O$  to be absorbed by the  $BaO$ , the residual gases being forced into a gas holder, and on the outward stroke the cylinder is filled with  $O$  under such pressure that at the next compression stroke a higher temp. is attained, sufficient to cause decompn. of the  $BaO_2$ , which decompn. is continued during

the expansion stroke by a suitable supply of heat; *N* is obtained in this process if a portion of the air from which the *O* has been removed, is subjected to retreatment; *H<sub>2</sub>O<sub>2</sub>* is obtained in this process if at the third stroke, *H* mixed with *H<sub>2</sub>O* vapor is introduced into the cylinder; *Cl* by the Deacon process—air is compressed, and at a suitable point of the compression stroke, *HCl*, and if necessary *H<sub>2</sub>O* is injected into the cylinder containing, as catalyst, pieces of clay satd. with *CuCl<sub>2</sub>*; *SO<sub>2</sub>* by the contact process—air alone, or mixed with *SO<sub>2</sub>*, is compressed to the necessary temp., and during the remainder of the stroke rise of temp. is obviated by the introduction of *SO<sub>2</sub>* or of air, suitably cooled; the *manuf. of NaOH*, by injecting during the compression stroke regulated quantities of an ammoniacal salt soln. into an atm. of compressed *CO<sub>2</sub>*.

**Electric cables.** H. DEBAUGE. Brit. 156,066, May 6, 1920. A cable having the usual core and India-rubber or gutta-percha insulation has an outer coating of felted material consisting of fibers such as cotton, hemp, wool, silk, asbestos, etc., ground up with rubber in a rubber mixer, powdered mineral and coloring-matters being added. The mass is applied by an ordinary tubular covering-machine.

## 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

**Bacteriological investigations of biological purification.** J. GROENEWEGE. *Mededelingen uit het Geneeskundig Laboratorium te Wellervreden* 3, 66-125(1920).—The first phase of the purification process is the bacteriological decompn. of the waste materials of animal and vegetable origin into org. acids, chiefly *AcOH*, butyric acid and smaller quantities of formic and higher fatty acids, and alcs., mainly *EtOH* and *BuOH*, together with *CO<sub>2</sub>*, *H<sub>2</sub>*, *NH<sub>3</sub>* and *H<sub>2</sub>S*. Since most of these products can be easily fermented to *CH<sub>4</sub>* in the lab. it may be expected that *CH<sub>4</sub>*-fermentation forms the predominant process of the second phase occurring in the septic tank. As in the lab. expts., the *CH<sub>4</sub>*-ferments accumulate in the sediment (sludge). The uniform flow of liquor through the septic chamber corresponds to the repeated decantation practiced in the lab. and new food is continually furnished to the bacteria while decompn. products such as *H<sub>2</sub>S* and *CO<sub>2</sub>*, which hinder *CH<sub>4</sub>*-fermentation, are carried off. An equil. is reached between the increase in bacteria by multiplication and the number carried off in the stream. The sources of the *H<sub>2</sub>* are (1) pectose-fermentation of the pectins by the butyric acid ferments yielding *CO<sub>2</sub>*, *H<sub>2</sub>* and volatile fatty acids, chiefly *AcOH* and butyric acid; (2) fermentation of glycerol, mannitol, dextrin, starch, etc., by butyric acid ferments yielding *AcOH* and butyric acid. Frequently alcs., chiefly *BuOH*, are formed. (3) Fermentation of certain compds., as glycerol, by aerobacteria, to org. acids, *H<sub>2</sub>* and *CO<sub>2</sub>*. Similarly *B. coli communis* ferments glucose and lactose to *H<sub>2</sub>* and *CO<sub>2</sub>*. (4) Fermentation of formates to *H<sub>2</sub>* and *CO<sub>2</sub>* by *Bacterium formicum*. (5) Fermentation of proteins. Much less *H<sub>2</sub>* is formed than is to be expected when any of the above substances is fermented in a flask after inoculation with septic-tank sludge. This is due to the formation of *CH<sub>4</sub>* by the *CH<sub>4</sub>*-ferments according to the reaction:  $4H_2 + CO_2 = CH_4 + 2H_2O$ . *CO<sub>2</sub>* is formed in *CH<sub>4</sub>*-fermentation and in all processes producing *H<sub>2</sub>*. The quantity found in the escaping gases is no criterion of that formed, since large quantities are dissolved and carried off in the out-flowing liquid. *N<sub>2</sub>* forms 3.4-64.9% of the escaping gases. The small amts. of nitrate and nitrite brought into the septic tank in the waste-liquor cannot account for the *N<sub>2</sub>* produced. Part of the *NH<sub>3</sub>* formed is directly consumed as food by bacteria. Another portion is converted by nitrifying bacteria present in the scum to nitrites. These diffuse in the liquid and are converted to *N<sub>2</sub>* by denitrifying bacteria. Nitrification is hindered or entirely stopped in absence of air or by too high a concn. of certain org. substances. No *N<sub>2</sub>* is, therefore,

formed in an air-tight septic tank. Nitrites, even in very small amts., hinder  $\text{CH}_4$ -fermentation and indirectly decrease  $\text{CO}_2$ -formation since much more  $\text{CO}_2$  is formed in  $\text{CH}_4$ -fermentation ( $\text{CH}_4:\text{CO}_2 = 3:1$  in acetate fermentation and  $\text{CH}_4:\text{CO}_2 = 5:2$  in butyrate fermentation) than in denitrification where the gases formed are chiefly  $\text{N}_2$ . Consequently less  $\text{CH}_4$  and  $\text{CO}_2$  occur in the gases of open septic tanks. The  $\text{H}_2\text{S}$  formed in the lower strata of the tank is oxidized by the nitrites in the upper strata with the formation of  $\text{S}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{SO}_4$ . This is of practical value since, in a properly operating open septic tank or a closed one with slight access of air, the escape of  $\text{H}_2\text{S}$  and consequent stench are excluded when there is sufficient diln. for the nitrite-formation.

ALBERT R. MERZ

**Filtration as an independent means of water purification.** F. B. LEOPOLD. *Pub. Works* 50, 296(1921).—There is given a brief historical summary of the water purification problem, the need of filtration being established, inasmuch as  $\text{Cl}$ , ozone and ultra-violet rays are only sterilizing and finishing agents.

LANGDON PEARSE

**Filtration plant recommended for Buffalo.** ANDREWS AND FULLER. *Pub. Works* 50, 264(1921).—Objectionable turbidity for at least 3 months per yr. is reported. Use of  $\text{Cl}$  is not regarded as sufficient. Rapid filters are recommended.

L. P.

**Chemical methods of de-aeration of water or solutions.** H. A. WHITE. *J. Chem. Met. Soc. S. Africa* 21, 105–11(1921).—As a means of removing  $\text{O}$  from cyanide solns. or from boiler feed water the value of the following substances was detd.:  $\text{FeSO}_4$ ,  $\text{MnSO}_4$ , tannin, all in the presence of lime. Tannin showed an efficiency practically 100% of the theoretical. Ferrous ammonium sulfate removed practically all of the  $\text{O}$  but destroyed half the cyanide and did not sep. out from soln. as is essential for com. working.  $\text{MnSO}_4$  gave an efficiency of 70–77%. As pure tannin is too costly, wattle bark ext. was tried with good results. A table is given showing the estd. costs of removing a pound of  $\text{O}$  from both boiler water and cyanide soln. Wattle bark ext. is the cheapest. Some work done on the rate of corrosion of  $\text{Fe}$  in  $\text{O}$ -free and  $\text{O}$ -containing waters seems to show a lessened corrosion in the  $\text{O}$ -free water.

E. H. D.

**Degassing and purification of boiler-feed water.** PAUL KESTNER. *Iron Coal Trades Rev.* 102, 364(1921).—K. discusses the process of continuous blowing down used in conjunction with hot purification. The latter effects a thermal saving and has the further advantage of eliminating gases dissolved in the feed  $\text{H}_2\text{O}$ . Also in *Engineering* 111, 291(1921).

S. D. K.

**Reports and notes of the public health laboratories, Cairo, 105 pp.** The manner of sampling and methods of analyses are given. Investigation shows that Nile River water does not exert an unduly high plumbo-solvency action and there is no danger from  $\text{Pb}$  poisoning. Use of supplementary alum before the water enters filters produces  $\text{CO}_2$  which causes corrosion of meters. Bleaching powder rapidly deteriorates in warm climates, but investigation shows that bleach dried in a current of  $\text{CO}_2$  retains its strength even better than when dried with quick-lime. Analyses of native alum deposits, statistics on prepn. of electrolytic hypochlorite, reports of inspections of water supplies and analyses of waters from the more important wells used as drinking supplies in Egypt and Sinai peninsula are given.

G. C. BAKER

**Waste water purification plant.** E. V. CHAMBERS. *Chem. Age (London)* 4, 250(1921).—Processes for the treatment of wastes from woolen industries and metal-working factories using "pickle" liquor are given. Screening of the woolen wastes is followed either by settling tanks, gravity filters or centrifugal filters to remove the suspended solids or sedimentation with the use of a coagulant to remove the colloidal material, depending upon the particular liquor being handled. The effluent is treated with  $\text{H}_2\text{SO}_4$  to neutralize the  $\text{CO}_2$  and set the oil free. Settlement for 12 hrs. follows, when the clear acid water is withdrawn and the oil is recovered from the magma by

passage through steam-heated filter presses. After extn. to remove the remaining oil the filter cake can be used as a fertilizer. In treating the "pickle" liquor enough  $H_2SO_4$  is added to set all the combined chlorine free as  $HCl$ , which is obtained by distillation. Iron is recovered as  $FeSO_4$ . Also in *Chem. Trade J.* 68, 305-6(1921).

G. C. BAKER

Sand filters for small sewage plants. W. A. HARDENBURGH. *Pub. Works* 50, 275(1921).—The practice of various state authorities is described. From 2 to 3 ft. depth of sand is recommended, with an allowance of 1 acre for 750 persons, or 100,000 gals. per acre per 24 hrs. Engineering details are given.

LANGDON PEARSE

Sewage treatment at Lexington, Ky. ANON. *Pub. Works* 50, 249-52(1921).—The plant serves 3,500 acres, population of 45,000, with an av. flow of 3 mil. gal. per 24 hrs. Included is a bar screen with a 2-in. opening, grit chamber (3 compartments), 2 Imhoff tanks (each 2 units), 2 dosing tanks (each 11,000 gal.) and 2 acres of sprinkling filters, 6 ft. deep. The sludge bed area is 12,600 sq. ft. in 6 beds. The annual maintenance cost has been \$4,249.00. Four hrs. time of one man keeps the nozzles clean. Fifty % of the sludge is carried away by farmers.

LANGDON PEARSE

Prevention of stream pollution by dye and intermediate wastes. E. J. CASSELLMAN. *Public Health Reports* 35, 187-85(1920).—Investigations were carried out as to properties and disposal treatment of several wastes of the dye and intermediate industries. Lab. studies were made of the properties of wastes from toluidine, nitrobenzene, ethylaniline and dyes and for lagoon liquor. Treatments that were cheaper than evapn. were found for the lagoon liquor, the ethylaniline wastes, and the lake-forming dye wastes; and a method of treating toluidine waste was indicated in lab. expts. For the lake-forming dye wastes and ethylaniline wastes the following treatment was recommended to a chem. company: (1) A mixt. together of all the wastes and wash waters except the waste and wash water from the manuf. of the "direct green" series of dyes. (2) Addition and dissolving of ferrous salt in the proportion of 1.2 lbs. of Fe per 1000 lbs. of soln. This can be done in a wooden vat. (3) Addition, with agitation, of slaked lime in the proportion of 8 lbs. of  $Ca(OH)_2$  per lb. of Fe (or 9.6 lbs. of  $Ca(OH)_2$  per 1000 lbs. of soln.). This amt. is in addition to the amt. necessary to neutralize the acid in the waste if any should occur. (4) Filtration with or without settling of the supernatant liquid. This can be done by means of a sand filter bed or any other suitable filtering medium. (5) Dln. of the effluent from the filter with 5 times its vol. of  $H_2O$ . Daily removal of the solid sludge from the filter to suitable dumps or hollows. The only satisfactory method found for disposal of "direct green" dye wastes is evapn. A systematic set of steps for exptl. treatment of wastes is appended.

JULIAN H. LEWIS

Toledo garbage disposal. ANON. *Pub. Works* 50, 263(1921).—The city is to pay \$1.25 per ton for disposal of garbage by reduction.

LANGDON PEARSE

Centrifuge (KELLNER) 1. Mixing (Brit. pat. 152,649) 1.

Treating feed-water for boilers; removing gases dissolved in liquids. W. S. ELLIOTT. Brit. 155,864, July 17, 1919. For removing from feed-water and other liquids the air and gases dissolved therein, the liquid, suitably heated, is arranged to flow downwardly into the vacuum chamber, in which the actual sepn. takes place, and to be maintained up to the moment of its entry under a positive head of liquid so that premature ebullition is obviated, and thereafter the heated liquid is subjected to a pressure lower than that corresponding to the temp. of the liquid so that the latter is caused suddenly to boil with explosive violence. In the case of feed-water,

removal of the gases leads to the sepn. of the carbonates in soln. A suitable construction is specified. Cf. *C. A.* 14, 305.

**Purifying water and sewage.** J. N. A. SAUER. *Brit.* 155,610, June 20, 1919. Impure  $H_2O$  and sewage are purified by treatment with finely divided high-class decolorizing C which has undergone a preliminary treatment. This consists in boiling the C with weak alkali or acid or heating to a high temp. in closed retorts or in a combination of such operations.

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

**Relation of the calcium content of some Kansas soils to the soil reaction as determined by the electrometric titration.** C. O. SWANSON, W. L. LATSHAW AND E. L. TAGUE. Kansas Agr. Expt. Sta. *J. Agr. Research* 20, 855-67 (1921).—Representative Kansas soils were tested for total Ca, Ca sol. in  $N HCl$  and in  $0.2 N HCl$  and for  $CO_2$ . The surface soils are grouped according to their  $p_H$  values. The hydrogen electrode app. used was the same as previously described (*C. A.* 13, 486). The initial  $p_H$  value and the number of cc. of  $0.04 N Ca(OH)_2$  required to produce a certain  $p_H$  value were detd. Similar data are given for subsoils. The subsoils have a higher Ca content than the surface soils and in most cases they require more  $Ca(OH)_2$  to change them to the same reaction than the surface soils require. The amt. of  $0.04 N Ca(OH)_2$  required to change a soil from a lower to a higher hydroxyl ion concn. depends more on the amt. of colloidal clay present than on the Ca content. Electrometric measurements in equivalents of  $CaCO_3$  per acre in 0 to 7 in. of the surface soil in comparison with the amt. of  $CaCO_3$  required by the Hopkins method are given. In some soils the amt. of  $Ca(OH)_2$  calcd. in equivalents of lbs. of  $CaCO_3$  per acre required to change to a concn. represented by  $p_H$  8.3 is equal to or more than the equivalent of the amt. of acid-sol. Ca present in the soil. F. C. COOK

**Thirty-ninth annual report, 1919-20. Chemistry.** C. E. THORNE. Ohio Agr. Expt. Sta., *Bull.* 346, 40 (1920).—(a) *Organic phosphorus.* The org. P in a number of soils showed no variation in nature, although the amt. present varied. Cultivation and cropping decreases the total and org. P and in practically the same ratio. As an av.  $\frac{1}{3}$  the total P of surface soils and  $\frac{1}{4}$  that of sub-soils is in org. combination. The evidence obtained does not indicate that the organically combined P of the soil is readily available. (b) *Effect of fertilizers on availability of rock phosphate as indicated by the P content of the oat plant.* Yield of oats was increased by rock phosphate. There was no indication that other fertilizers affected the availability of rock phosphate. The P content of the oat plant was greater than where the crop was grown without rock phosphate. The most decided effect was obtained when the oats were sampled 8 weeks after seeding. (c) *Sulfur in relation to soils and crops.* S increased the acidity of soils and the availability of certain mineral constituents but did not increase the yield of corn, oats, wheat, soy beans, potatoes and clover in exptl. plots. (d) *Potassium supply of soils.* The concn. of K in the soil soln. varies appreciably depending on the soil texture and the treatment. The sol. K content of unfertilized soil is greater than that of soil where the treatment has caused increased yields. Ca and acid phosphate had a pronounced effect on the removal of available K in this manner from a silt loam soil. J. J. SKINNER

**Automatic method for mechanical soil analysis and ways of recording it.** SVEN ODEN. *Bull. Geol. Inst. Univ. Upsala* 16, 15-64 (1919); cf. *C. A.* 13, 1198.—Exact mechanical soil analysis is difficult because of the dependence on temp. and uniformity of sample. It is measured through the behavior of particles of soil falling in a liquid.

Theoretically the velocity of particles may be expressed as  $V = Cr^2$  (Stokes law), where  $C$  is a const. equal to  $(2/9)g(\sigma - \sigma_1)/\mu$ ; where  $g$  is the const. of gravitation,  $\sigma$  the sp. gr. of the particles and  $\sigma_1$  that of the liquid and  $\mu$  the size of particle. This equation is based upon the supposition that the size of particles does not exceed a certain critical radius ( $85\mu$  for quartz). As particles usually have different forms it is necessary to introduce a radius of equivalence for particles. The medium radius of equivalence for a certain amount of soil should then be equal to the medium size of particles in suspension. If medium sp. gr. of soil be placed at 2.7 and  $\mu$  be given as 0.0114 at  $15^\circ$  in abs. measure, the const  $C$  in an aq. suspension should equal  $5.546 \cdot 10^{-2}$ . This const. will vary with  $\mu$ , which again varies very much with temp. If a substance varying in size is suspended in a liquid: (1) Velocity of accumulation is proportional to the total amt. of the substance and reciprocally proportional to the height of the liquid, but independent of time. (2) If  $v_i$  is the velocity of particles of size  $i$ , then an equal amt. each of particles of smaller size will sink down in the time interval 0 to  $h/v_i$ . For carrying out expts. O. used a glass cylinder 35 cm. high and 138 mm. inside diam. filled with water. Inside of this and near the bottom a gold-plated silver plate is hung up by strings in the water. The substance to be analyzed is let in on top of the cylinder and a certain amt. is collected on to the plate, which again is connected with an automatic balance. When this balance is upset an elec. current closes releasing small steel shot, which again equal the wt. of collecting particles on the scale. The steel shots have to be uniform and are chosen in 4 sizes weighing, resp., 0.4386 g., 0.1276 g., 0.0544 g., 0.0133 g. Velocity of accumulation is thus closely detd. and recorded on a recording app. attached to the balance. After expts. are made and recorded the number of particles is counted with the ultra-microscope after the method of Zsigmondy-Siedentopf. A falling curve may be shown in a diagram with the amts. of particles  $g(r)$  as ordinates and the radii of equivalence  $r$  as abscissas. Graphically this may be shown by the integration of a function  $F(r)$  between  $r_1$  and  $r_2$ :

$$g(r_2) - g(r_1) = \int_{r_1}^{r_2} (dg/dr) dr = \int_{r_1}^{r_2} F(r) dr.$$

$F(r)$  represents here the curve of distribution of the particles and this may be calcd. from the above formula. Sometimes particles will coagulate, the falling curve then differing slightly from the ordinary one. The curve of distribution is calcd. and shown in a diagram, where ordinates and abscissas are represented, resp., by the logarithms of  $dP/dt$  and of  $t$  ( $P$  = weight of particles).  $N$  is number of particles and being a function of  $r$   $N(r)$  is called function of frequency. Tables and diagrams show results obtained with Danish Rhaet Ler and mica-clay from Venid. Three photographs are given of cylinder, automatic balance and recording app., resp. **Preliminary treatment of soil in mechanical analysis.** *Ibid* 125-34.—In different soils individual particles are often combined into aggregates differing from the primary particles. In preliminary treatments such aggregates are broken up, all particles being reduced to primary ones. Normal method for treatment: The material is brushed with a stiff brush when in distd. water; then the larger particles are removed in a centrifuge and the material is brushed again. Enough  $\text{NH}_3$  is added to give a 0.01  $N$  soln. and the whole is mixed in a machine for 24 hrs.  $\text{NH}_3$  breaks up aggregates especially well for soils containing Ca salts, NaCl, KCl and  $\text{MgCl}_2$ . Boiling breaks up aggregates also but produces coagulation afterwards; it is therefore not advisable to boil.

G. N. KIRSEBOM

Clay of Ancyus. SVEN ODÉN AND A. REUTERSKIÖLD. *Bull. Geol. Inst. Univ. Upsala* 16, 135-58(1919).—Expts. were carried out on this clay according to methods

given by Odén (preceding abstr.). The clay of Ancyus was geologically detd. as Post-Glacial sweet-water sediment formed in the intermediary period, when the Baltic Sea was shut out from the Atlantic, forming the Ancyus lake, so-called after the mollusk *Ancyus fluviatilis* found in the sediment. Mechanical analysis detd. the size of particles to be between 0.17 and 7.0 $\mu$ . Chemically the particles differ in compn. according to size, the larger ones being richer in silica. Samples were dissolved in strong HCl to find the action on the particles. Results are given of different size fractions before and after treatment with acid, av. size of particles and their number being detd. Fractions taken were <0.23 $\mu$ , 0.23–0.60 $\mu$ , 0.60–1.05 $\mu$  and 1.05–5.13 $\mu$ . In the original sample 33.5% was undissolved. Action of acid was strongest on the fraction around 0.4 $\mu$ . Av. size of particles increased in smaller fractions but decreased in larger ones. Tables show results of mechanical tests and a graphic table indicates the influence of HCl on chem. compn.

G. N. KIRSEBOM

Development during the war, of the methods of producing ammonia and nitrates. ANON. *Compt. rend. agr. France* 7, 58–62(1921).—Production statistics are given. The paper shows how products of war times may be converted to peace time uses as fertilizers, etc. Methods of producing explosives are very briefly discussed.

F. M. SCHERTZ

Improving calcium cyanamide. H. G. SÖDERBAUM. *Kungl. Landbruks-Akademien Handlingar och Tidskrift* 59, 511–7(1920).—During the war N from CaCN<sub>2</sub> was practically the only form obtainable in fertilizers. CaCN<sub>2</sub> has the following drawbacks: (1) It is a plant poison and the N must be changed to other forms before it can be used by plants. (2) The N in it has a lower value and its action is slower than in the case of nitrates or NH<sub>4</sub> salts. (3) It cannot be used as a top dressing as it must be applied to the soil sometime before seeding. (4) It is dusty and difficult to get on the land. (5) It is changed to stony hardness by dampness and some N is lost. How to overcome these drawbacks economically is the problem. The simple chem. process of taking up water by which CaCN<sub>2</sub> is first changed to urea and then to NH<sub>3</sub> offers a soln. While the fertilizer value of NH<sub>4</sub> salts is well known, that of urea is not and exptl. evidence is conflicting. To test the fertilizing value of urea, S. grew oats in pots, using a sandy soil deficient in N. N in equal amts. from 4 preps. was applied to the different pots: (1) c p. urea, (2) technical, once crystd., (3) technical, (4) urea + CaCO<sub>3</sub>. NaNO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> were used as checks. The basic fertilizer was composed of K<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, NaCl and Thomas phosphate. The results showed that urea is as effective a carrier of N as NaNO<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Differences were within exptl. error.

C. O. SWANSON

Potash shales of Illinois. S. W. PARR AND M. M. AUSTIN. III. Agr. Expt. Sta., *Bull.* 232, 229–36(1921).—Shale occurs in Union Co., Ill., containing 5% K<sub>2</sub>O. It has chem. and phys. characteristics which render it suitable for use in making Portland cement. The southern Ill. shale contains free oil, bituminous matter, pyrite, undecomposed K-bearing rock, and K-bearing material of the nature of glauconite or greensand. Extn. of K by means of reagents seems impractical. By means of pot expts. the shales are shown to be beneficial to plant growth. *Geology, distribution, and occurrence of the potash-bearing shale of Union County.* FRANCIS KREY. *Ibid* 237–43.—Finely ground shale as a source of potassium for soil improvement. ROBERT STEWART. *Ibid* 244–52.—In a series of pot expts. working with a limed peat soil, a comparison of kainite, alunite, leucite, roasted alunite and shale was made. Leucite and roasted alunite proved beneficial. Shale produced larger growth than did kainite or the other sources of K used. Rape, beets, flax, clover, buckwheat and corn were used in the expts.

J. J. SKINNER

**Nitrification of barnyard manure added to sour peat soil.** CHR. BARTHEL AND N. BANGTSSON. *Kungl. Landbruks-Akademiens Handlingar och Tidskrift* 59, 518-33 (1920).—The authors used a sour peat soil cultivated over 40 years. On the dry basis it analyzed 80% volatile matter and 2.53% N. It was strongly acid,  $p_H$  being 5.44. The tests were made in 5 to 6 l. pots closed with paraffined stoppers. Access of air was provided by means of glass tubes filled with cotton. To different pots were added, resp.:  $(NH_4)_2SO_4$ ,  $(NH_4)_2SO_4 + CaCO_3$ , manure, manure +  $CaCO_3$ , manure +  $(NH_4)_2SO_4$ , manure +  $(NH_4)_2SO_4 + CaCO_3$ . There were check pots besides. Samples were taken from the pots periodically and the dry matter, nitrates and  $NH_4$  were detd. The rate and amt. of nitrification is compared with that of neutral and sour clay soil previously investigated. The nitrification in sour peat soil, both with and without the addition of  $(NH_4)_2SO_4$ , proceeded as rapidly as in neutral clay soil. Not only did the N from the manure undergo nitrification, the same as with mineral soils, but also some of the N from the peat was nitrified. The addition of lime to sour peat soil increased the nitrification of  $(NH_4)_2SO_4$  to a greater extent than it did in sour clay soil, but it had no influence on the nitrification of N from the manure. In this respect this sour peat soil acted similarly to neutral or sour mineral soil. The addition of  $(NH_4)_2SO_4$  to the sour peat soil increased the  $p_H$  value from 5.4 to 4.0 after which it remained const. This high H-ion concn. did not hinder nitrification. C. O. S.

**Action of chloropicrin on higher plants.** G. BERTRAND. *Compt. rend.* 170, 858-60 (1920); cf. Guérin and Lormand, *C. A.* 14, 3445.—Leafy stems or branches of many of the common trees, shrubs and herbs, the latter representing annuals, biennials and perennials, were cut, immediately placed in small flasks filled with water and submitted to an atm. containing known amts. of chloropicrin which varied from 1 to 200 g. per cu. m. Temp. was 15 to 20° and the action of chloropicrin was observed in both darkness and light. With the stronger concns. the leaves were quickly killed and in a measure fixed. Instead of withering they preserved almost their original forms up to complete desiccation upon the branch. With weaker concns. (20 g. per cu. m.), strong plasmolysis was observed, the droplets appearing upon the surface of the leaves. The green color became darker and more bluish or sometimes reddish or even entirely red like autumnal tints. Following this the leaves became yellow, brown or black according to the species, then withered and fell. With a few g. of chloropicrin per cu. m. the dominant effect was plasmolysis. The leaves wither and nearly always fall off as if affected by cold or anesthetics. Along with plasmolysis induced by chloropicrin there is generally the disengagement of odors, which is attributed to the hydrolysis of glucosides, such as bitter almond from cherry-laurel, new mown hay from melilot, etc. Adult leaves are more sensitive to the toxic action than young leaves. Some days after defoliation by chloropicrin, the unaltered buds develop and cover the plant with new leaves. It is possible that with care chloropicrin may be used to rid plants of foliaceous parasites. Cf. following abstr. L. W. RIGGS

**Action of chloropicrin on parasites of wheat and on rats.** A. PIUTTI. *Compt. rend.* 170, 854-6 (1920).—P. gives a report of his work in collaboration with L. Bernardini (*Rend. r. accad. sci. Napoli* 23, 5, 24, 16) on the action of chloropicrin. His papers were published previously to those of G. Bertrand and others on the same subject. The conclusions of both investigators are in practical agreement. P. recommends a much lower concn. of the toxic agent, viz., 20 cc. per cu. m. of wheat. Rats on two naval vessels were exterminated by chloropicrin in concns. much lower than those used by Bertrand (1.5 kg. per 1875 cu. m. of space). Cf. preceding abstr.

L. W. RIGGS

**Further (information) on limestone and American vines.** G. DE ANGELIS D'OSSAT. *Staz. sper. agrar. ital.* 53, 97-100 (1920).— $CaCO_3$  detns. were made on 30 samples of



soil taken from the surface and at depths of 0.5 m. and 1.0 m. at 10 points of a plot. Results were:

	1	2	3	4	5	6	7	8	9	10
Surface.....	28.16	24.25	28.85	35.43	27.89	26.46	30.70	27.81	31.71	33.68
0.5 m.....	27.34	31.97	33.01	33.52	31.27	31.63	35.43	33.40	40.35	32.00
1.0 m.....	28.50	27.50	40.76	45.00	32.73	32.83	34.90	31.42	31.06	30.02
Vines were grown in 14 rows (arrangement shown by plate) on this plot which measured 18 m. × 7 m. These vines can endure the % CaCO <sub>3</sub> mentioned below according to Bonnet's scale.										
Row 14. Bonnet scale, 37.51%.	<i>V. Berlandieri</i> ( <i>aculeata</i> ). Slightly chlorotic.									
Row 13. Bonnet scale, 22.5%.	<i>V. Candica</i> × <i>Riparia</i> × <i>Rupestris</i> ( <i>Solonia</i> ). Very vigorous without any chlorosis.									
Row 12. Bonnet scale, 15.0%.	<i>V. Rupestris</i> ( <i>Forthworth</i> ). Vigorous, free from chlorosis.									
Row 11. Bonnet scale, 15.0%.	<i>V. Riparia</i> <i>vigorisissima</i> of Avellina. Luxuriant vegetation.									
Row 10. Bonnet scale, 17.5%.	<i>V. Riparia tomentosa</i> . Vigorous vegetation.									
Row 9. Bonnet scale, 12.0%.	<i>V. Riparia glabra</i> . Vigorous vegetation.									
Row 8. Bonnet scale, 15.5%.	<i>V. Riparia tomentosa</i> . Vigorous vegetation free from chlorosis in non-trimmed plants.									
Row 7. Bonnet scale, 17.5%.	<i>V. Riparia</i> . Vegetation average.									
Row 6. Bonnet scale, 15.0%.	<i>V. Rupestris</i> of Avellina. Very vigorous vegetation.									
Row 5. Bonnet scale, 5.0%.	<i>V. Labrusca</i> × <i>aestivalis</i> . Very vigorous vegetation.									
Row 4. Bonnet scale, 10.0%.	<i>V. Labrusca</i> × <i>Riparia</i> (Clinton). Vegetation average. Chlorotic.									
Row 3. Bonnet scale, 5.0%.	<i>V. Labrusca</i> (Isabella). Vegetation good. Free from chlorosis.									
Row 2. Bonnet scale, 22.5%.	<i>V. Vinifera</i> × <i>aestivalis</i> (Jacquez). Vegetation limited. Slightly chlorotic.									
Row 1. Bonnet scale, 45.0%.	<i>V. Vinifera europaea</i> . Vegetation vigorous.									

The most striking differences between the old theory and the facts are: No. 3. *V. Labrusca*. This plant which should endure not more than 5% CaCO<sub>3</sub> grows without chlorosis in a soil the limestone content of which varies between 30.02 and 40.35%. No. 5. *V. Labrusca* × *aestivalis*. This plant, although also assigned 5% CaCO<sub>3</sub>, nevertheless grows most vigorously in a medium containing 27.81-35.43%. No. 8. *V. Riparia tomentosa* (Bonnet 15.5%). Endures 32.83%. No. 11. *Riparia vigorosissima* (15%). These two plants grow without chlorosis, the first with 26.49-32.83% CaCO<sub>3</sub>, the second with 22.34-40.76%. Other expts. on different fields confirmed the absolute lack of correlation between facts and the proposed theoretical scales. These results are all in line with those obtained by A. d'O. (C. A. 9, 1953). ALBERT R. MERZ

**Cotton fertilization experiments—1920.** F. H. SMITH AND T. S. BUIR. Georgia Agr. Expt. Sta., *Bull.* 137, 36(1920).—In a field expt. 4 kinds of P rock were compared: 2 from Tennessee and 2 from Florida. The yields from these did not vary widely. When composted with org. ammoniates better results were obtained. Favorable results were obtained with the natural phosphates the first year. J. J. SKINNER

**Fertilizer.** M. O. JOHNSON. U. S. 1,370,117, Mar. 1. A fertilizer in the form of compressed cakes containing vegetable fibrous and fruity material and coagulated vegetable proteins is prepd. from waste fruit juice and pulp, *e. g.*, that from pineapples.

**Fertilizer from vegetable refuse.** A. C. ZIRWAS AND D. DONOVAN. U. S. 1,369,871, Mar. 1. Vegetable refuse is subjected to the action of liquid stable products.

**Fertilizer.** P. RADMANN. Norw., 30,974, Aug. 9, 1920. A mixt. of alkali-bearing rock or weathered material, gypsum and limestone (preferably 0.25—1 part gypsum and up to 3 parts limestone to 1 part rock) is broken down at a temp. of 1000–1250° (below the m. p. of the mixt.) and then comminuted in a disintegrator. The mass then constitutes a fertilizer in which the fertilizing action exceeds that of ordinary fertilizer mixts. both as to lime and sol. K salts, and total plant food, and it is therefore applicable directly as an artificial fertilizer. Cf. C. A. 14, 2675.

**Fertilizer.** WETCARBONIZING, LTD. Ger. 321,859, Oct. 30, 1915. Peat, wet-carbonized under pressure, is subjected to the action of gases containing  $\text{NH}_3$ . Generator gas or gases obtained from peat carbonized in the wet state under pressure, may also be used. Claim is made that by the action of ammoniacal gases on the wet-carbonized peat a chem. combination of the  $\text{NH}_3$  results, due to the acid formed in the free state during wet-carbonizing, independent of the free acid which is added to aid in the wet-carbonizing process.  $\text{NH}_4$  salts are formed.

**Mechanical preparation of a soft product from hard mineral tricalcium phosphate.** COMPAGNIE DES PHOSPHATES DE CONSTANTINE. Norw. 30,975, Aug. 9, 1920. The phosphates are first crushed in such manner that the soft and hard granules which always form a part of every natural phosphate remain intact, while the less resistant portions containing  $\text{CaCO}_3$  and poor in  $\text{P}_2\text{O}_5$  fall to an impalpable powder. The material is then treated in a revolving, preferably horizontally mounted drum provided interiorly with a screw which moves and lifts the mass so that it falls continuously upon side ribs in the drum. By this treatment the soft granules are sepd. from the gang by abrasion, while the resulting dust is blown by a current of air into a separator. The material here seps. according to its wt. into 2 sorts, the soft granules with high  $\text{P}_2\text{O}_5$  content, and the low grade material containing  $\text{CaCO}_3$ , in which the  $\text{P}_2\text{O}_5$ , on account of the fineness of the powder, is sol. in citric acid.

**Disintegration of mineral phosphates for fertilizer manufacture.** E. STOPPANI AND V. VOLPATO. Ger. 321,776, Jan. 22, 1916.  $\text{CaCO}_3$ , about 6% by wt. of the phosphate mixt., is added to the latter, the mixt. is heated to about 600° at most, and after heating the mass is treated with  $\text{H}_2\text{O}$ . In this manner, and without the employment of a higher temp. sufficient to fuse the material, and large amts. of additions reducing the phosphoric acid content, the production of a fertilizer containing the acid in available form is claimed.

**Calcium cyanamide.** J. H. LIDHOLM AND DETTIFOSS POWER CO., LTD. Ger. 321,618, Mar. 19, 1913. In the manuf. of  $\text{CaNCN}$  by the action of N on  $\text{CaC}_2$  under pressure and at an elevated temp., the rise of the reaction temp. to fusion or sintering of the  $\text{CaNCN}$  is prevented by the addition to the  $\text{CaC}_2$  of an indifferent substance such as sand or the like. The degree of dilution of the  $\text{CaC}_2$  with sand or the like is dependent upon the pressure, and can be readily determined for each type of furnace and batch of carbide. With a pressure of 5–10 atm., the dilution should be 40–45%.

## 16—THE FERMENTATION INDUSTRIES

H. S. PAINE

The utilization of Jerusalem artichokes in the distillery. KARL WINDISCH. Z. *Spiritussind.* 43, 292, 300(1920); cf. Rüdiger, preceding abstr.—The tubers of the artichoke contain, chiefly, instead of starch, inulin and its degradation products. Enzymes which can hydrolyze inulin are found in some molds (*Penicillium aspergillus*) and yeasts (*S. marxianus*, *S. exiguus*, *S. pombe*). Inulinase is not present in malt.

The chief product of hydrolysis is levulose, and another carbohydrate present, levulin, is easily fermentable. The av. compn. of the tubers was found to be as follows: water, 77.7; N, 0.34; protein, 2.10; fat, 0.14; crude fiber, 1.33; N-free ext., 17.68; ash, 1.05. A number of fermentations was made with a brewer's yeast after varying treatments, resulting in 0-10 l. of alc. per 100 kg. of raw material, averaging 8 l. The highest yields were obtained from the raw mash, not steamed or treated with malt. Acid hydrolysis raises the yield, but is said to be too delicate for small distilleries. A large-scale expt. in a distillery confirmed the yield of 8 l. of alc. per 100 kg. Com. fermentation of this material, however, is now forbidden in Germany. W. B. VAN ARSDALE

**Fermentation process for the production of acetic and lactic acids from corn cobs.** E. B. FRED AND W. H. PETERSON. *J. Ind. Eng. Chem.* **13**, 211-3 (1921); cf. C. A. **15**, 1147, 1150.—Three successive hydrolyses of 100 g. of corn cobs in an autoclave at a steam pressure of 15 lbs. and temp. of 121° gave 30.9 g. of sugar calcd. as xylose. The first hydrolysis with 0.5% of H<sub>2</sub>SO<sub>4</sub> for 10 min. gave 2.2 g. sugar; the second with 2% H<sub>2</sub>SO<sub>4</sub> for 1 hr. gave 18.5 g. and the third with 2% H<sub>2</sub>SO<sub>4</sub> for 1 hr. gave 10.2 g. The sirups prepd. from these hydrolyses after diln. with yeast water until the concn. of sugar reached about 2% were inoculated with *Lactobacillus pentoceticus* n. sp. and incubated 2 weeks at 30°. The total yields were 14.8 g. AcOH, of which 12.6 g. were produced by pentose fermenters, and 16.4 g. lactic acid, 13.8 g. of which resulted from fermentation processes. About 86% of the sugar present was accounted for by these two products. The fermented solns. showed only slight traces of unfermented xylose. The fermentation of untreated cobs (100 g.) gave about 1 g. each of these acids. These expts. show that every ton of corn cobs would be capable of yielding 300 lbs. of AcOH and 320 lbs. of lactic acid. In the U. S. there are produced annually more than 20,000,000 tons of corn cobs. G. W. STRATTON

**Alterations in a top-yeast grown on a galactose substrate.** H. v. EULER, I. LAURIN AND A. PETTERSSON. *Biochem. Z.* **114**, 277-91 (1921).—It was found by expt. that the quotient 1:50 represents the normal relation between the fermentation capacities of a sample of top-yeast towards cane sugar and galactose between the 2nd and 5th hours of fermentation. The fermentation of galactose was retarded by the addition of an aq. ext. of dried yeast. When the top-yeast was previously treated with galactose soln. it was possible to change the quotient of the relation of the fermentation velocities between cane sugar and galactose from 1:50 to 1:6.5. F. S. HAMMETT

Yeast crops (SLATOR) 11C.

**Antiseptic for sake.** H. SHIOIRI. Japan 36,471, May 31, 1920. Lactic acid is used safely as an antiseptic for 180 l. of sake.

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

**A contribution to the study of civette.** JEAN NIVIÈRE. *Bull. soc. chim.* **27**, 794-7 (1920).—Analytical data obtained in the examn. of 4 samples of civette are presented. These samples, contained benzene-insol. material to the extent of 6.6, 6.4, 7.0 and 8.3%. In one case, the insol. residue yielded 18.35% of ash consisting of talc. The other samples gave only traces of ash. The residue obtained on evapg. the benzene was sol. in alc. to the extent of 56.70, 57.01, 55.21 and 38.82% on the original civette. Acid nos. of this alc.-sol. material are given as 103.1, 106.3, 109.0 and 111.0; the ester nos. 15.3, 22.1, 19.4 and 25.2; the sapon. nos. 118.4, 128.4, 128.4 and 136.2. The chem. constants of the alc.-insol. portion of sample No. 2 are: Acid no. 8.4, ester no.

69.7, sapon. value 78.1, I value 68.43 and acetyl value 80.02. Cholesterol was identified in the alc.-insol. portion, scatole and the capric and caprylic acid salts of ethyl- and propylamines in the alc.-sol. portion, and glucose in the benzene-insol. residue.

A. G. DUMAZ

**Evaluation of neosalvarsan.** A. KIRCHER AND F. VON RUPPERT. *Ber. pharm. Ges.* 30, 419-21 (1920).—The method is based upon that described by Norton and Koch (*J. Am. Chem. Soc.* 27, 1247 (1905)).

W. O. E.

**Pharmaco-flora of the Ssemiretschensk district in Turkestan.** E. SWIRLOWSKY. *Ber. pharm. Ges.* 30, 474-80 (1921).

W. O. E.

**Estimation of cineole in essential oils.** C. KLEBER AND W. v. RECHENBERG. *J. prakt. Chem.* 101, 171-7 (1920).—The method is based on the solidification point of the sample, pure cineole solidifying at +1.2°. A table has been prep'd. at which various concns. of cineole solidify; thus, beginning with 100% cineole, the solidification points down to 64% are, resp.: +1.2, +0.8, +0.3, -0.2, -0.7, -1.2, -1.7, -2.2, -2.7, -3.3, -3.8, -4.3, -4.8, -5.3, -5.8, -6.4, -6.9, -7.4, -8.0, -8.6, -9.2, -9.7, -10.3, -10.6, -11.5, -12.2, -12.8, -13.5, -14.1, -14.8, -15.4, -16.1, -16.7, -17.4, -18.2, -18.9, -19.6°. In a double-walled vessel (2 test tubes of varying diameter may constitute the system) introduce 5-10 cc. of the sample and supercool in a NaCl-ice mixt., finally bringing the mass to solidification by rubbing the side of test tube with the thermometer or by inoculation with a minute crystal of cineole. Remove from the cooling mixt. and stir with the thermometer until rise in temp. ceases. This does not, however, constitute the final point of observation, since the true f. p. is the temp. at which the crystn. just begins or disappears. Accordingly the oil is made to melt and then only moderately cooled, whereby after a few trials the solidification point is noted within tenths of a degree. Oils containing less than 65% cineole are naturally difficult of detn., as for example cajuput oils, which contain about 60% cineole. In such cases the sample may be mixed with an equal amt. of cineole and the detn. effected as above. The lowest value found was -10.5°, most of the samples thus prep'd. solidifying at -8 and -9°, equivalent to 77.5-82% for the mixture, or 55-64% for the original oil.

W. O. E.

**Cresineol method for the determination of cineole.** C. E. SAGE AND J. D. KITTLE. *Perf. Essent. Oil Rec.* 12, 44-6, (1921).—With a view to finding the relationship between the wt. of cineole phosphate and the vol. of cineole which it yields, the wts. of the pressed cake of phosphate obtained in many detns. before decomp. it with H<sub>2</sub>O have been observed, with the result that a mean multiplication factor of 0.588 was developed, which, applied to the wt. of cineole phosphate cake obtained, affords a rapid means of predicting the vol. of cineole which will result from its decomp., and moreover, obviates the necessity of measuring the cineole, thereby saving much time in cases where the distinct sepn. of the 2 layers of liquid is tardy. Use of the theoretical factor 0.611 leads to the reporting of high results.

W. O. E.

**Essence of Hinojo Dulce.** C. E. SAGE. *Perf. Essent. Oil Rec.* 12, 46, (1921).—Samples of sweet fennel oil have recently appeared on the market which have their source in entire plants of Spanish origin, rather than the fruits only. The absence of anethole in any notable quantity shows the product to be entirely different from that distd. from the fruit of *Foeniculum vulgare*, and suited only for flavoring purposes or in the prepn. of some liquors. The oil possessed the following characters:  $d_{44}^{20}$  0.9203 and 0.9340,  $d_{20}^{25}$  1.4945 and 1.4980, optical rotation +46 and +24, soly. in 90% alc. 1 in 1, still liquid at -15°, in the case of 2 samples exam'd. It is suggested that such products be termed "plant" oils in distinction to "fruit" oils usually prep'd.

W. O. E.

Peru balsam and its adulteration. L. VAN ITALLIE. *Am. J. Pharm.* 93, 24-6 (1921).—See C. A. 15, 921. W. G. GAESSLER

Pharmaceutical research. GEORGE M. BERINGER. *Am. J. Pharm.* 93, 132-42 (1921).—A review. W. G. GAESSLER

Iodine monochloride. E. FOURNEAU AND E. DONARD. *Bull. sci. pharmacol.* 27, 561-6(1920); cf. C. A. 15, 920.—The addition of NaCl stabilizes solns. of ICl to the same degree as does HCl; it is more convenient than HCl and does not inhibit the 1st phase of the ICl<sub>3</sub> decompn. which yields ICl. The use of ICl as an antiseptic in medicine and surgery is strongly advocated. Brief discussion is given of the various methods of prep. ICl and detg. its strength in soln. The method employed is based on the soly. of free I<sub>2</sub> in CHCl<sub>3</sub>, which does not dissolve ICl to any great extent, and on the facts that ICl and its compd. with HCl are very sol. in Et<sub>2</sub>O and the ICl liberates I<sub>2</sub> from KI acting as 2 active Cl atoms. Shake 1 cc. of the soln. to be tested 3 times with 10 cc. abs. Et<sub>2</sub>O, add 20 cc. of 10% KI and 2 cc. HCl to the Et<sub>2</sub>O ext. and titrate with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The result should be checked by gravimetric detns. of I and Cl. The titrimetric method, while not very exact, is sufficient for ordinary purposes. F. S. HAMMETT

Study of potassium guaiacolsulfonate (Thiocol). C. A. GRAU. *Bull. sci. pharmacol.* 27, 566-76(1920).—A tabular report of the analyses of some ten commercial preps. labeled as K guaiacolsulfonate, accompanied by general conclusions drawn from the series of papers as a whole, of which this is the last. Cf. C. A. 14, 952. F. S. HAMMETT

Endocrine gland extracts: their manufacture and use. S. G. STRAUSS. *N. Y. Med. J.* 113, 395-7, 468-9(1921).—The excessive demand for pituitary products has necessitated the importation of raw materials from the slaughter houses of the Argentine. (The effect of this lapse of time between removal of the gland and its extraction is of doubtful value. Reviewer.) The paper discusses the various methods of drying, defatting and general prepn. for market. It is interesting to note that 5 lbs. of fresh pituitaries are obtainable from 1000 head of cattle; for the pineal 2000 head of cattle are required for the same amt., and 50 sheep supply 1 lb. of fresh thyroid. The only 3 preps. which are standardized are the posterior lobe of the pituitary, the thyroid and the ext. of the medulla of the suprarenals, e. g., adrenaline. There is nevertheless a great variability in the strength of the exts. as found on the market. The thyroid is standardized according to the I<sub>2</sub> content. Thymus is obtained from sheep or calves: orchitic substance from rams and bulls; ovarian extract from cows or sows; corpus luteum substance from pregnant cows or sows. In all of these preps. deterioration occurs. It is suggested that the mfrs. announce the exact nature of their products in all its detail so that therapeutic results may be better understood and thereby stabilized. F. S. HAMMETT

An alkaloid of *Sinomenium diversifolius*. NISABURŌ ISHIWARI. Kyoto Imp. Univ. *Chūgai Iji Shimpō*. No. 959, 1-20(1920).—Stems and roots of *Sinomenium diversifolius* (Miq.), Diels were heated with twice as much 95% alc. on a water bath for several days. After distn. of the solvent, the residue was purified with Pb acetate and extd. with Et<sub>2</sub>O in acidic soln. By making alk. with Na<sub>2</sub>CO<sub>3</sub>, and extg. the mother liquor with Et<sub>2</sub>O, an alkaloid, C<sub>16</sub>H<sub>19</sub>NO<sub>5</sub>·H<sub>2</sub>O, white needles, m. 161°, was isolated. It was named *sinomenin* (a different alkaloid, cocculinum, C<sub>17</sub>H<sub>19</sub>NO<sub>5</sub>·3H<sub>2</sub>O, was formerly isolated from the same plant: Taguchi and Ōta, Tokyo Iji Shinshi, 1919). It is easily sol. in acids, alc., CHCl<sub>3</sub>, Me<sub>2</sub>CO, and amyl alc., moderately in Et<sub>2</sub>O and C<sub>6</sub>H<sub>6</sub>, difficultly in H<sub>2</sub>O, giving alk. soln., but not in petroleum ether. Hydro-

chloride, white prisms, m. 224°; picrate, yellow plates, m. about 140°. The pharmacol. action of the hydrochloride for frogs, mice and rabbits resembles that of quinine.

K. K.

The composition of hops. I and II. YOSHITAKA HASHITANI. *J. Soc. Agr. Forestry, Sapporo* 12, 1-11, 97-114(1920).—A review.

K. K.

Testing Swedish *Scopolia carniolica*. N. O. ENGFELDT AND G. LILJESTRAND. *Svensk Farm. Tidskr.* 25, 53-62(1920).—The roots of *Scopolia carniolica*, which occurs in several parts of Sweden, were analyzed according to the methods given in the Pharm. Helv. and U. S. P., also by that recently published by Rapp (*C. A.* 15, 574). The last method was unsatisfactory owing to the soly. of the acids and alkalies in the  $\text{CHCl}_3$ . The other 2 methods gave results that agreed very closely, i. e., 0.342 and 0.340%. In following the procedures of the Helv. method there should be exercised extra care in the 3 evapns. with  $\text{Et}_2\text{O}$  in order to be sure that all the  $\text{NH}_3$  is removed. The roots contained 7.56% ash. The alkaloid when isolated gave  $[\alpha]_D = -25.7^\circ \pm 2.5^\circ$ . Pharmacol. tests were made on the central nervous system of frogs, isolated living segments of rabbit intestine, and the pupil of the cat. The action was identical with that of *l*-hyoscyamine. When compared with atropine in the above tests the two were similar and in the last test the alkaloid from the Swedish roots were found to be almost twice as active as atropine.

A. R. ROSE

The investigation of salvarsan. Utz. *Pharm. Zentralhalle* 62, 65-7(1921); cf. *C. A.* 15, 145.—The white ppt. and the red-brown color which develop when perhydrol is used to destroy the org. part of salvarsan are not necessarily indicative of the presence of the latter. However, their absence may indicate adulteration. H. A. SÄÖNLE

Colloidal properties of arsphenamine in aqueous solution. Z. KLEMMENSIEWICZ. *Bull. soc. chim.* 27, 820-4(1920).—The viscosity of aq. solns. of arsphenamine was measured by the ordinary capillary flow method. It was found to increase for some time after the prepn. of the soln. The rate of increase was more rapid for concd. than for dil. solns. When concd. solns. were dild. the viscosity did not sink immediately to the normal value. This behavior may be accounted for by the assumption that the arsphenamine is present in the form of colloidal particles more or less hydrated. Solns. that had been heated for several hrs. out of contact with O, when cooled, had a much lower final than initial viscosity. This is probably due to chem. decompn. during the heating.

E. B. SPEAR

Mexican herbs and drugs. E. M. HOLMES. *Chemist and Druggist* 94, 40-1 (1921); *Pharm. J.* 106, 17(1921).—A descriptive and critical review is given of about 25 out of 70 Mexican drugs on exhibit in London by the Overseas Trade Dept. A much exported bark merely labelled "Tlalxalac" contained much tannin. "Estafiate" (*Artemisia mexicana*, Willd.) is a source of santonin (cf. *C. A.* 15, 924), and might be cultivated in the tropical colonies. Some typical Mexican drugs were not included, and the lack of expert knowledge in the selection is regretted.

S. WALDBOTT

Dispensing notes. HAROLD WYATT. *Chemist and Druggist* 94, 315-7(1921).—A symposium of more or less difficult prescriptions, including nitrites in mixts., insol. powders, incompatibilities, and prescriptions in foreign languages.

S. WALDBOTT

The aconitine content of some samples of alcoholature of aconite leaves. R. RICHAUD. *J. pharm. chim.* 23, 15-6(1921).—Detn. of aconitine by Bertrand's (official) method in 4 samples of reliable origin showed variations from 0.139 to 0.409 g. per 1000 g., confirming results of Écalle (1902). Either a standard should be fixed for this prepn. as has been done for the tincture, or preferably the prepn. should be dropped.

S. W.

Solubilization of terpin in therapeutic doses. GALAVIELLE, CRISTOL, AND PORTES. *J. pharm. chim.* 23, 51-6(1921).—Lactic acid is found to be the best solv nt for terpin previously dehydrated; 1.5 cc. official acid dissolves 1 g. terpin when the mixt.

is heated to 84° (terpin m. 105°). On cooling and diln. with H<sub>2</sub>O, the soln. as a rule remains clear; if it ppts., heat to boiling; on cooling no crystn. was noted during 25 days. Or, add the hot mixt. of the above amts. (the therapeutic doses per day) to 50 cc. of cold H<sub>2</sub>O; to the well stirred colloidal soln. add 70 cc. of lemon sirup or gooseberry sirup. If terpin hydrate be used (also 1 g.), crystn. is prevented for at least a few days by adding 3 cc. of rum to the 50 cc. of cold H<sub>2</sub>O. To avoid the astringent effect of the lactic acid, prescribe milk, or alk. waters, or simply NaHCO<sub>3</sub> for the intervening hrs. S. W.

**Cascara sagrada (Rhamnus purshiana DC.) grown in Scotland.** ALEXANDER McCUTCHEON. *Pharm. J.* 106, 72-3(1921).—Description is given of the planting and transplanting of a specimen grown from seed of American origin 15 yrs. ago. The plant is thriving in absence of any special cultural attention. A fluidext. made of the bark of the twigs was fully equal in its physiol. action to that made from com. bark.

S. WALDBOTT

**Cultivation of medicinal plants in Scotland, past and present.** R. GLOBE GUYER. *Pharm. J.* 106, 146-9, 168-71, 190-2(1921); cf. *C. A.* 14, 2968.—A detailed history of the Edinburgh early "medicine" gardens is given, with the biography and portrait of their founder Sir Robert Sibbald (1641-1722), and an account of their development under James Sutherland and others. Then a detailed report, with photographs, is made of the following crops grown since 1915 at Warriston by Duncan, Flockhart & Co.: Aconite, belladonna, colchicum, digitalis, henbane, poppies, roses, stramonium and valerian. Aconite root in 1920 gave 0.69% alkaloids; belladonna leaves up to 0.58%, roots 0.72-0.78%; hyoscyamus 0.082% calcd. as hyoscyamine. Minor crops grown were: broom, calendula, conium, chamomiles, dandelion, elder, fennel, juniper, licorice, timothy grass and veratrum; also Scottish roots of male fern were collected, yielding oleoresin with over 30% of filicin.

S. WALDBOTT

**Medicinal plant cultivation at Inverness (Scotland).** DONALD MITCHELL. *Pharm. J.* 106, 232-3(1921); cf. preceding abstr.—M. relates an ancestor's experience in growing medicinal plants in 1808-1860.

S. WALDBOTT

**Laboratory notes on (a) double salt of quinine with sulfuric acid and acetylsalicylic acid, (b) narcophine, (c) morphine methochloride.** D. B. DOTT. *Pharm. J.* 106, 232(1921).—(a) The soly. of quinine sulfate (A) being about 1 in 800 of H<sub>2</sub>O, that of acetylsalicylic acid (C) 1 in 400, a mixt. of A and C is more sol. than either. A max. soly. is obtained in the ratio of 4 mols. of C to 1 mol. of A. On evapn., uniform crystals were obtained having the compn. B<sub>2</sub>H<sub>2</sub>SO<sub>4</sub>·4C<sub>9</sub>H<sub>8</sub>O<sub>4</sub>·4H<sub>2</sub>O, (B = C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>). Its soly. is 1:50. The max. amt. of H<sub>2</sub>O of crystn. is 9 mols., decreasing to 4H<sub>2</sub>O by efflorescence. After drying over H<sub>2</sub>SO<sub>4</sub>, it m. 96°. (b) Narcophine (D) is morphine narcotine meconate, C<sub>17</sub>H<sub>19</sub>NO<sub>3</sub>·C<sub>22</sub>H<sub>23</sub>NO<sub>7</sub>·C<sub>7</sub>H<sub>7</sub>O<sub>7</sub>·4H<sub>2</sub>O; also with 6H<sub>2</sub>O. At 140° gas is given off; m. 168° with further decompn. (Narcotine, m. 176°, morphine m. 247°.) D is sol. (incompletely) in 5 parts H<sub>2</sub>O; like caffeine, it is a weak base whose org. salts are decomposed by H<sub>2</sub>O. Meconic acid may be heated on the water bath to const. wt., losing only 3H<sub>2</sub>O, or 2H<sub>2</sub>O, while in boiling water it loses CO<sub>2</sub> forming comenic acid. (c) The compd. (E) forms prisms from H<sub>2</sub>O, compn. B·MeCl<sub>2</sub>·2H<sub>2</sub>O. 1 H<sub>2</sub>O is lost below 100°, the other at 135-140°. The salt is sol. in 10 parts H<sub>2</sub>O and in 160 parts of 90% EtOH (W/V). With FeCl<sub>3</sub>, HNO<sub>3</sub> and HIO<sub>3</sub> it reacts like morphine salts, but its physiol. action is radically different. With NaOH it forms methyl morphinehydroxide, not morphine; no ppt. is formed with Na<sub>2</sub>CO<sub>3</sub> or NH<sub>4</sub>OH, while its acidified soln. gives a bulky cryst. ppt. with K<sub>4</sub>Fe(CN)<sub>6</sub>; morphine salts yield no ppt. After drying on the waterbath E m. 285° with much decompn. D. recommends the use of H<sub>3</sub>PO<sub>4</sub> in place of H<sub>2</sub>SO<sub>4</sub> or paraffin for m. p. detns. near 300°.

S. WALDBOTT

**A photosensitive mixture of bismuth. Preliminary note.** E. G. BRYANT. *Pharm. J.* 106, 233(1921).—A mixt. containing KBr 15 grains, liq. bismuthi et Ammon. citr-

1 drachm.  $\text{NaHCO}_3$  15 grains, oil of peppermint 1 minim, Aq. chlorof. to make 0.5 ounce was markedly sensitive to light. A black mirror, turning white again in the dark, was formed on the side exposed to even moderate sunlight. In the absence of  $\text{NaHCO}_3$ , light seemed to have no visible effect.

S. WALDBOTT

**Henbane cultivation.** E. M. HOLMES. *Pharm. J.* 106, 248-9(1921); cf. T. W. Hazelby, *ibid* 106, 227.—The successful cultivation of henbane from seeds requires proper selection and treatment of the seed and treatment of the soil. Dried seeds fail to germinate at all. H. finds that on sowing the whole of the seeds of a biennial plant, the crop will be a mixt. of several sizes; reject the small, brown, immature seeds floating on  $\text{H}_2\text{O}$  when dry; others, small and gray, yield annual, the larger size biennial plants. From annual plants, seeds yielding the biennial, are obtained by proper thinning out and at first removing the flowering shoots. The ash of the plant contains  $\text{P}_2\text{O}_5$  44,  $\text{MgO}$  21,  $\text{K}_2\text{O}$  18,  $\text{CaO}$  6,  $\text{Na}_2\text{O}$  5%. The excess of  $\text{MgO}$  over  $\text{CaO}$  explains the preference of the plant for the seashore and magnesian inland soils.

S. WALDBOTT

**Bismutum subnitricum.** M. C. TRAUB. *Schweiz. Apoth. Ztg.* 58, 526(1920).—In the soly. test of Bi subnitrate with "dil.  $\text{H}_2\text{SO}_4$ ," the amt. of  $\text{H}_2\text{SO}_4$  directed in Pharm. Helv. IV is insufficient. This is due to the error of adopting the wording of the Germ. Pharm. IV whose dil.  $\text{H}_2\text{SO}_4$  is stronger. The directions should read: "0.5 g. basic Bi nitrate should be completely sol. at ordinary temp. and without effervescence in 42 cc. dil.  $\text{H}_2\text{SO}_4$ ."

S. WALDBOTT

**Modified salicylic acid and Samarin.** ANON. *J. Am. Med. Assoc.* 76, 883(1921).—These products are sold by the Frank S. Betz Co. of Hammond, Ind. Modified salicylic acid is claimed to be "acid salicylic so treated as to render it non-irritating to the stomach." The product is marketed in tablets, the av. wt. of which is 0.3843 g. or about 5.9 grains. Analysis gave acetylsalicylic acid, 81.5,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  9.2, talc (acid-insol.) 0.7 and starch, 8.6%. Each tablet contains about 4.8 grains of acetylsalicylic acid, and half a grain each of gypsum and starch with traces of talc. No information concerning the compn. of Samarin is given by the mfr. It is marketed in the form of tablets, the av. wt. of which is 0.3597 g. or about 5.5 grains. Analysis gave acetanilide 37, Ca salicylate 32,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  7, talc (acid-insol.) 6 and starch (by difference) 18%. The presence of acetanilide is not declared on the label. Each tablet is equiv. to about 2 grains of acetanilide and nearly 1.5 grains of salicylic acid.

L. E. WARREN

**Tablet manufacture.** ROBERT C. WHITE. *J. Am. Pharm. Assoc.* 9, 788-801 (1920).—Historical and descriptive essay.

L. E. WARREN

**Purity standards for absorbent cotton.** A. WAYNE CLARK, R. O. SMITH AND LEROY FORMAN. *J. Am. Pharm. Assoc.* 9, 958-65(1920).—The methods and standards of the U. S. P. IX and of the U. S. Army are described and criticized. No satisfactory method for the detn. of  $\text{H}_2\text{O}$  absorbability is known. The published methods are crude.  **$\text{H}_2\text{O}$  ext.** The described method is recommended. Place 10 g. of cotton in 200 cc. of boiling  $\text{H}_2\text{O}$  in a porcelain dish. Boil 5 min., pressing the cotton with a glass rod. Press out 100 cc., add 50 cc. of cold  $\text{H}_2\text{O}$  and press out 50 cc. Repeat the cold- $\text{H}_2\text{O}$  treatment twice. Evap. the united washings. The wt. should not exceed 0.25%.  **$\text{EtOH}$  ext.** In the U. S. P. method 10 g. of cotton are packed tightly in a percolator and extd. with  $\text{EtOH}$  until 100 cc. have been obtained. By this method, after 15-20 min. percolation, 0.155% was obtained but 2 further extns. with 50 cc. each of  $\text{EtOH}$  gave 0.05 and 0.02% more. By allowing 45-50 min. for the percolation, a residue of 0.22% was given and 2 additional extns. gave 0.03 and 0.02 % additional. By extn. for 8 hrs. in a Soxhlet app. the ext. amounted to 0.47% and 2 hrs. more extn. 0.015% additional. By long-continued extn. by the percolation method values as high as by the Soxhlet method may be obtained but the process is time-consuming.  **$\text{Et}_2\text{O}$  ext.** By extn. for 6 hrs. by the Soxhlet method, 0.44% was obtained. Other methods tried gave less,



but by using a large amt. of solvent values sufficiently accurate for control work may be obtained. Ext. 10 g. with  $\text{Et}_2\text{O}$  until 200 cc. have been obtained. On evapn. the residue does not exceed 0.6%.  
L. E. WARREN

Glycerol (ROBB) 27. Determination o the purity of spermaceti (BORISCH, KÜRSCHNER) 27. A new calcium salt (GAUCHER, ROLLIN) 10. Arsenical ompounds related to arspenamine (RAIZISS, GAVRON) 10.

Disinfectant. C. J. BABB. U. S. 1,370,263, Mar. 1. The strength of pine oil as a disinfecting agent is preserved (by preventing its oxidation into non-disinfecting compds.) by mixing it with invert sugar or other reducing agents, *e. g.*, H, CO,  $\text{SO}_2$ , sulfites or hypophosphites.

Synthetic drugs. FARBWERKE VORM. MEISTER LUCIUS & BRUNING. Brit. 155,577, Nov. 30, 1920. Stable solns. are obtained by mixing solns. of 3,3'-diamino-4,4'-dihydroxyarsenobenzenesulfoxylate and the Na salt of 3,3'-diamino-4,4'-dihydroxyarsenobenzene or the complex Ag compd. thereof, or by mixing the 2 ingredients in powder form and dissolving the mixt. The resulting soln. contains the 2 ingredients in chem. combination; that made from the Na salt is not pptd. by  $\text{CO}_2$ , and that made from the Ag compd. is not pptd. by NaCl or  $\text{CO}_2$ .

Theobromine derivatives. SOC. CHIMIQUES DES USINES DU RHONE, ANCIENNEMENT GILLARD, P. MONNET ET CARTIER. Brit. 155,748, May 27, 1920. Dialkylaminoethyl derivs. of theobromine are prepd. by the interaction of chloroethylalkylamines with a metallic salt of theobromine. By the addition of the requisite amt. of mineral acid, the neutral salt of the base, *e. g.*, the hydrochloride, can be obtained.

Thiophene derivatives. H. SCHRIEBLER. Brit., 155,546, Dec. 17, 1920. Addition to 155,259 (C. A. 15, 1139). The process of prep. oils containing thiophene derivs. described in the principal patent is modified by additional treatment of the oils at 100–110° with Na, sodamide, or Na and dry gaseous  $\text{NH}_3$ . After distn. *in vacuo* the oils require only small amts. of alkyl Mg halide for the final treatment, or this latter may be omitted entirely. The products have medicinal value.

Antiseptic deodorizer. M. ONO. Japan 36,932, March 25, 1920. Tar, obtained by dry distn. of rice-bran, oil cake and wheat-bran, etc., is washed 2–3 times with hot water, dissolved in an equal amt. of soap, mixed with half a part of Japanese pepper (*Xanthoxylum piperitum*, DC.) oil and 33 parts cold  $\text{H}_2\text{O}$ .

## 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

The manufacture of sulfuric acid in the United States. A. E. WELLS AND D. E. FOGG. Bur. Mines, *Bull.* 184, 216 pp.(1920).—The extent of the  $\text{H}_2\text{SO}_4$  industry is reviewed and the various uses of the acid are given quant. Next in order are taken up the raw materials, equipment and methods for manufg. chamber acid and concg. it, and for contact acid; and a brief résumé of the leaching and sintering of pyrites cinder. The amount of chemical engineering data given is unusually large. F. C. Z.

The Benker-Millberg system for the intensive manufacture of sulfuric acid. ANDRÉ COCHET. *Industrie chimique* 8, 93–7(1921).—The distinctive feature of the system consists in the use of 2 lead chambers after the Glover tower, operating in parallel, the combined vol. of which is the same as that of the lead chamber in the ordinary systems. For the proper working of the Gay-Lussac towers the temp. of the gases must be relatively low, so that all the heat of reaction and much of the sensible heat of the gases must be eliminated through the walls of the chambers. In the B.-M. system

the cooling surface of the double lead chambers, where most of the acid is produced, is approx. 11% greater than that of an equiv. single chamber; hence at a given working temp. the output is greater, and for a given output the temp. of the chamber walls, and consequently the deterioration of the Pb, are lower. The output depends largely on the mean velocity of oxidation of  $\text{SO}_2$  in the lead chamber. This is greater in the B.-M. system owing to the slower velocity of flow of the gases in a double chamber than in a single chamber, though the initial velocity of reaction is the same in both. Hence to increase the output in the case of a single chamber, the initial rate must be increased much more than with a double chamber, resulting in higher temp. and deterioration of the Pb. The last chamber may also be advantageously replaced by 2 smaller ones. The B.-M. system allows of great reduction in output, as one of the lead chambers can be entirely removed from the circuit, thereby giving exceptional flexibility. The importance of proper filtration of the spray water and of having suitable nozzles is briefly dwelt upon.

A. P.-C.

The Alsatian potash industry. HENRI VIGNERON. *Chem. Met. Eng.* 24, 655-61 (1921).

E. H.

Salt, bromine and calcium chloride in 1919. HERBERT INSLEY. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part II, 239-56 (preprint No. 16, published Mar. 26, 1921).

E. H.

Fuller's earth in 1919. JEFFERSON MIDDLETON. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part II, 257-64 (preprint No. 17, published Mar. 9, 1921).

E. H.

Mica in 1919. HERBERT INSLEY. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part II, 269-77 (preprint No. 19, published Mar. 28, 1921).

E. H.

Glass paper. RASSER. *Kunststoffe* 10, 121-2, 139-40 (1920).—A general description of the manuf.

C. J. WEST

Separation of two salts having a common ion (SCHLOESING) 2. Causticization of sodium sulfate (NEUMANN, KARWAY) 6. Effecting chemical reactions (BRIT. PAT. 155,776) 13.

Phosphorus and phosphoric acid. R. YASUDA. Japan 36,361, May 11, 1920. P is prepd. by heating a mixt. of  $\text{Ca}_3\text{P}_2\text{O}_8$  100,  $\text{AlPO}_4$  100 and charcoal (90% C) 48 in an elec. furnace at 1500-1600° according to the equation:  $2\text{AlPO}_4 + \text{Ca}_3\text{P}_2\text{O}_8 + 10\text{C} = \text{Al}_2\text{O}_3 + 3\text{CaO} + 4\text{P} + 10\text{CO}$ . Phosphoric acid is prepd. by passing the burned product of the above mixt. into  $\text{H}_2\text{O}$ .

Ammonia. SOUTH METROPOLITAN GAS CO. Ger. 321,661, Apr. 21, 1914. In the production of  $\text{NH}_3$  by the hydrolysis, by means of acid ( $\text{H}_2\text{SO}_4$ ), of the  $\text{NH}_4\text{SCN}$  obtained from the HCN contained in unpurified coal-gas, the hydrolysis is effected at a temp. not over 50° and under such conditions, to be detd. by special preliminary tests, that no noticeable ppt. appears in the liquid in the reaction vessel and no considerable amts. of volatile nitrogenous products escape. For the hydrolysis an amt. of  $\text{H}_2\text{SO}_4$  is used which is equiv. to the  $(\text{NH}_4)_2\text{SO}_4$  formed by the hydrolysis and the  $\text{NH}_3$  from the gas vol. from which the thiocyanate has been formed. The liquid formed during hydrolysis is used in the satn. vessel for the production of  $(\text{NH}_4)_2\text{SO}_4$ . An  $\text{NH}_4\text{SCN}$  soln. of 25-30% and a  $\text{H}_2\text{SO}_4$  70-80% are employed; 1 vol. thiocyanate soln. is heated with 1.5 vol. acid to 80-110°. The hydrolytic action proceeds in the sense of the equation:  $\text{NH}_4\text{SCN} + \text{H}_2\text{O} = \text{COS} + 2\text{NH}_3$ .

Aluminium hydroxide. R. S. SHERRWIN. Brit. 153,352, July 8, 1919. In the pptn. of  $\text{Al}(\text{OH})_3$  from alkali aluminate soln., only the finer particles of  $\text{Al}(\text{OH})_3$  are added, the fineness of the particles being such that they remain more or less freely

suspended in the liquid; by the use of these fine particles the relative pptn. surface is increased, and if they are obtained by sepn. from the coarser particles of the pptd. hydroxide a less dusty product is obtained on calcination of the latter.

**Synthetic ammonia.** NITROGEN CORPORATION. Brit. 155,592, Dec. 20, 1920. A catalyst for the synthesis of  $\text{NH}_3$  consists of an alkali or alk.-earth metal Fe cyanide, *e. g.*,  $\text{K}_4\text{Fe}(\text{CN})_6$  or  $\text{Ca}_2\text{Fe}(\text{CN})_{10}$ , distributed upon a porous support, such as pumice. The catalyst is "activated" by gradually raising the temp. to about  $360^\circ$  in the presence of a N-H mixt. at atm. pressure and then slowly raising it to a temp. of about  $450^\circ$  in the contact chamber, while a mixt. of N and H under a pressure of 100 atms. is passed in until the issuing gas contains no trace of HCN. The temp. is not allowed to rise above the limits specified until the close of the activation process, when it may be allowed to remain at  $600^\circ$  for a short time. The synthesis of  $\text{NH}_3$  is then begun, the N-H mixt. under a pressure of 100 atms. being introduced into the contact chamber maintained at  $450^\circ$ . When the catalyst becomes spent, it may be blown out of the contact chamber by means of a jet of the working gases.

**Continuous production of ammonia.** R. W. WALLACE AND E. WASSMER. Ger. 321,817, Aug. 10, 1913. A metal, *e. g.*, Mg, Al, Ti, is treated with N to form a nitride, and then with suitable reagents, such as  $\text{H}_2\text{S}$  or HCl, to split off  $\text{NH}_3$ . For the regeneration of the metal from the nitride two salts are formed which, electrolyzed together, yield pure metal and at the same time the elements from which the salts can be subsequently again formed. If Mg metal is used, the nitride is treated with HCl at the ordinary temp.

**Stannic chloride.** S. OCHI AND THE TOKYO INDUSTRIAL RESEARCH LABORATORY. Japan 36,392, May 18, 1920.  $\text{SnCl}_4$  is prepd. by passing  $\text{Cl}_2$  into a mixt. of 500 g. Sn and 20 g.  $\text{S}_2\text{Cl}_2$  heated at  $100^\circ$ . When the Sn is dissolved away, the content is distd. and then boiled with 30 g. anhydrous  $\text{SnCl}_2$  and distd. again to eliminate the accompanying  $\text{S}_2\text{Cl}_2$ . The residue is used for the second operation. The catalyzer ( $\text{S}_2\text{Cl}_2$ ) can be replaced by S and Sn by  $\text{SnS}_2$ ,  $\text{SnCl}_2$  or  $\text{SnO}$ . In this operation, slightly moist  $\text{Cl}_2$  is used safely.

**Mercuric chloride.** K. OZEKI. Japan 36,433, May 25, 1920.  $\text{HgCl}_2$  is prepd. by heating a mixt. of 1 vol. powdered realgar or other substance contg. above 50%  $\text{HgS}$ , 0.5 vol. cryst.  $\text{MgCl}_2$  or solid bittern and 0.5 vol.  $\text{MnO}_2$  at  $350^\circ$ , whereupon  $\text{HgCl}_2$  sublimes.

**Recovering borax from saline waters.** G. B. BURNHAM. U. S. 1,370,278, Mar. 1. Saline waters such as Searles Lake brine which contain Na, K, Cl,  $\text{SO}_4$ ,  $\text{CO}_3$  and borate ions are evapd. to crystallize out Na, K, Cl,  $\text{SO}_4$  and  $\text{CO}_3$  salts and increase the concn. of borate ions and the remaining liquor is then cooled to crystallize out borax. Cf. C. A. 14, 804.

**Catalytic production of nitrogen-oxygen compounds from ammonia and air or oxygen.** PERMUTIT-AKT.-GES. Ger. 298,981, May 2, 1915. The gas mixt. is conducted over aluminate-silicate substances in which either the Al alone is replaced by one or more elements whose oxides are sol. in alkali, or the alkali is simultaneously or solely replaced by one or more heavy metals. In order to operate by means of Na chromite silicates, about 50 g. of the air-dried catalyzer are charged into a glass tube 50 cm. in length and 0.8 cm. diam., and a mixt. of  $\text{NH}_3$  and air, at a red heat, is conducted there-over, the mixt. containing about 2-5%  $\text{NH}_3$ . For the absorption of the resulting products several absorption tubes may be used, charging them successively with  $\text{H}_2\text{O}$ , lye and permanganate. If only 200 cc.  $\text{NH}_3$ , with the corresponding amt. of air, are led within  $1\frac{1}{2}$ -2 hr. over the heated catalyzer, 97-98% of the  $\text{NH}_3$  are claimed to be converted into N oxides of which about 60-65% are found as free acid in the aq. and alk.

absorption liquids. The conversion of  $\text{NH}_3$  in like manner can be effected by means of Cr aluminate silicates.

**Nitrogen oxides from air.** F. I. DUPONT. U. S. 1,370,295, Mar. 1. Mixed O and N are brought under the action of an elec. arc and the treated gases are cooled in 2 stages, one as the gases escape from the arc and the other at some distance from the arc. Gases which have been subjected to the second cooling are used as the cooling agent in the initial cooling. Gases escape outwardly from the arc and as they escape are given a whirling movement by the action of a current of the previously cooled gas. An app. is described.

**Mercuric oxide.** ELEKTRIZITÄTWERK LONZA. Norw. 30,998, Aug. 16, 1920. The oxidation of the metallic Hg is effected by means of gases containing O, in the presence of dry N oxides as O carrier.

**Carbon disulfide.** K. P. McELROY. U. S. 1,369,825, Mar. 1. Fuel such as coal, coke or charcoal is passed downward through a shaft under gas producer conditions, with introduction of air at the base of the shaft while S is introduced into the latter. Gases and vapors evolved are scrubbed with oil to collect  $\text{CS}_2$ .

**Sulfur.** J. J. HOOD. Brit. 155,692, Oct. 25, 1919. S from the spent oxide of gas-works or other analogous sources is purified by agitating a soln. of it in  $\text{CS}_2$  with  $\text{H}_2\text{SO}_4$ , whereby the greater part of the contaminating tarry matters is pptd., and then adding a small quantity of  $\text{H}_2\text{O}$  with thorough agitation to ppt. the remaining impurities. After filtration or decantation, the soln. may be passed through ignited bauxite or  $\text{Al}_2\text{O}_3$  as described in 140,844 (C. A. 14, 2242), and finally evapd. down for recovery of the S. For a less complete purification the bauxite treatment may be omitted.

**Apparatus for expelling sulfur dioxide in smoke as sulfur.** K. IKEDA and A. IWAMURA. Japan 36,316, May 5, 1920. The app. is composed of many small chambers, having rotating wings. Smoke containing  $\text{SO}_2$  is passed into the chambers with a corresponding quantity of  $\text{H}_2\text{S}$  and exposed to continuous flow of  $\text{H}_2\text{O}$ , by which  $\text{SO}_2$  is changed to S and  $\text{H}_2\text{O}$ .

**Apparatus for regenerating waste nickel catalyzer.** K. ÔMIYA and SUZUKI CO. Japan 36,355, May 10, 1920. The app. is composed of 3 rotating tubes heated electrically in which a helical conveyor is attached for spreading the catalyzer. Cleaned Ni catalyzer (cf. Japan 36,200, C. A. 15, 1414) is continuously reduced by  $\text{H}_2$  passed in opposite direction to the catalyzer moving in descending temp.

**Permanent paste.** M. SAITÔ, J. WATANABE and T. NAKAYAMA. Japan 36,310, May 4, 1920. Mixt. of starch 280 and powdered rice 60 is gradually mixed with 0.001%  $\text{H}_2\text{SO}_4$ , 800, 7% boric acid 300 and 10% alum soln. 200 and warmed to paste on a water bath under agitation.

**Polishing and cleansing composition.** H. S. BLACKMORE. U. S. 1,369,878, Mar. 1. A mixt. adapted for polishing and cleansing floors or other surfaces is formed of  $\text{C}_{10}\text{H}_7\text{Cl}_4$  or other halogen deriv. of  $\text{C}_{10}\text{H}_8$  and a non-viscous neutral mineral oil.

**Plastic compositions.** KOLN-ROTTWEIL AKT.-GES. Brit. 156,095, Dec. 22, 1920. A compn. suitable for floor coverings, etc., consists of nitrocellulose mixed with a gelatinizing agent, preferably non-combustible, such as tricresyl phosphate or amyl *p*-toluenesulfonate, together with cellulose material such as cork, sawdust, peat, and coloring and filling matter. In an example, 350 parts nitrocellulose containing 100 parts  $\text{H}_2\text{O}$  are mixed with 140 parts tri-*o*-cresyl phosphate, 140 parts secondary xylydine, 300 parts cork or sawdust, 100 parts mineral coloring matter and 50 parts chalk, and the mixt. is kneaded in a vacuum at  $75^\circ$  until the  $\text{H}_2\text{O}$  is removed. The product is pressed or rolled with the aid of heat.

**Horn-like substance from sea-weeds.** T. TANAHASHI, S. TAKAHASHI and K. WATANABE. Japan 36,202, April 15, 1920. Sea-weeds are treated with 0.1% HCl, washed, warmed with 10 times as much 1% NaOH or 2% Na<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>SO<sub>4</sub> at 60°, filtered, neutralized with 0.5% H<sub>2</sub>SO<sub>4</sub> or HCl, producing a ppt., which is bleached with Cl<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>, washed, sepd. from H<sub>2</sub>O, coagulated with 1% formaldehyde, immersed in 40% formaldehyde for several days and dried at room temp. Or, the ppt. is treated with lime water, 10% Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, alum or metallic acetate soln. and coagulated with formaldehyde soln.

**Emery cloth, etc.** TURK GNS. Brit. 155,754, Dec. 21, 1920. The fabric to which the emery or other abrasive powder is applied is formed by weaving cellulose yarn made of fibrous paper pulp or like material, which, being devoid of fat, adheres to the glue or other adhesive employed to secure the abrasive to the fabric.

**Elastic plate.** Y. TERASHIMA. Japan 36,317, May 5, 1920. Fine wood powder is mixed with a gasoline soln. of raw rubber and extended to a plate or painted on a cloth and dried.

**Indicating heating.** C. TIEDERMANN. Brit. 155,574, Nov. 24, 1920. To indicate heating of railway-vehicle axle or other bearings, the bearing is coated with a substance which changes color when hot and returns to its original color on cooling. An oil paint comprizing a Hg-I-Cu combination may be used, this being red when cool and black when hot.

**Condensation products from aldehydes and urea, etc.** H. JOHN. Brit. 151,016, Sept. 14, 1920. See C. A. 15, 418.

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

**Dissolved gases in glass.** EDWARD W. WASHBURN, FRANK F. FOOTITT and ELMER N. BUNTING. Univ. of Ill. Eng. Expt. Sta., *Bull.* No. 118, 32 pp.(1921).—The existence of dissolved gases in considerable quantities in a piece of perfectly clear barium flint optical glass was demonstrated by the method of "sudden evacuation." The glass was melted at atm. pressure in a vacuum furnace. At about 1200° the furnace was connected with a large evacuated tank. The furnace cooled under a pressure of less than 1 cm. of mercury. When the furnace was opened most of the glass was found outside of the pot, in the form of a large white mass of foam. The increase in vol. of the mass was about 6 times the vol. of the original piece. A special app. for both measuring and for analyzing the dissolved gases was developed. The furnace consisted of a Pyrex glass tube 5 × 13 cm. with ground glass stopper, containing a porcelain melting pot wound with Pt wire. Twenty-five or 50 g. of glass were introduced into the pot and after removal of adsorbed moisture the temp. was raised to 1400° and maintained until the manometer reading was steady. An Orsat app. was used to analyze the evolved gas for CO<sub>2</sub> and O<sub>2</sub>, residual gas being considered N<sub>2</sub>. The accuracy of the chem. analysis was about 1%. The 3 glasses investigated were barium flint optical glass, light flint bulb glass and boro-silicate lab. glass.

Glass	Volume % S. T. P.				Weight %			Conc. moles in per liter.			
	O <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	Total	O <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	Total	O <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>
Barium flint	83	27	<1	110	0.035	0.011	....	0.046	0.033	0.011	....
Light flint	36	12	<1	48	0.015	0.0045	....	0.020	0.016	0.005	....
Boro-silicate	4.5	10	3	18	0.0045	0.014	0.0025	0.021	0.004	0.010	0.003
Water at 0° C.	6	5	6	17	0.0036	0.0035	0.0031	0.010	0.0028	0.002	0.0028
	..	..	..	..	..	..	..	..	0.0023	0.080	0.0010

The quantity and nature of the gases present in finished glass obviously depends upon the batch compn. and the melting and finishing procedures. It is not probable that any appreciable quantities of gas are absorbed from the furnace atm. except possibly in the case of glasses which are stirred mechanically for a long period. The authors hint at possible applications in the construction of high-vacuum scientific app. and technical operations in machines using the vacuum gathering principle. A vacuum furnace process for the manuf. of certain types of glass is possible on an industrial scale. It offers the advantages that the fining operation is eliminated, the finishing temp. reduced, and glass is produced absolutely free from even the smallest seeds. W. M. C.

**Silica glass.** G. FLUSIN. *Chimie & industrie* 3, 729-49(1920).—In this article complex relations existing among the various forms of silica, cryst. and amorphous, are discussed in detail. Amorphous silica is the form stable at high temps., quartz being converted to silica glass by rapidly heating above 1470°, tridymite at 1670° and cristobalite at 1625–1710°. Silica glass on being heated for some time at 1500° devitrifies, owing to recrystn. to cristobalite. Conversion to tridymite is brought about by heating to 900–1470° in the presence of KCl. Fused quartz is very viscous even at temps. well above its melting point. It begins to volatilize rapidly at 1750°, while it is still pasty, so that it is very difficult to obtain silica glass free from bubbles. The following physical properties of silica glass are given: d. 2.21, coeff. of expansion  $49 \times 10^{-8}$ , sp. heat 0.20–0.28, heat of fusion (by calcn.) 64–6 g. calories per g. It is transparent down to  $\lambda = 0.220 \mu$ ;  $n_D$  1.4585, dispersion 0.0068, resistivity at 15–150°,  $2 \times 10^8$  megohms per cm., at 800° 20 megohms, modulus of elasticity 6.6 kg. per mm<sup>2</sup>. Silica glass is permeable to gases, especially to H and at high temps. It is not appreciably sol. in water even at 100°, nor in strong acids except hydrofluoric and phosphoric. It is not attacked by salt solns. but is appreciably sol. in alkalis, especially when hot. It reacts with metallic oxides as CuO when heated to 900°. J. S. LAIRD

**The mechanical properties of porcelain.** E. ROSENTHAL. *Keram. Rundschau* 29, 81–2, 93–4(1921); cf. C. A. 15, 1062.—The strength of porcelains may be divided into 2 classes: (1) resistance to static pressure, i. e., to a load applied slowly and (2) resistance to impact, i. e., to pressure applied suddenly. The compression and tensile strengths are detd. in the customary manner. The torsion strength, which heretofore has never been detd., is about 430 while that of cast Fe is 2228 and of cement 35.7 kg. per sq. cm. The velocity of transmission or vibration of sound varies with the modulus of elasticity. Those porcelains having the highest velocity are the best. This velocity may be increased by increasing the clay content. Also pure light burning clays give better results than impure clays. The impact tests are made by the Marten method by letting a pendulum drop on the test pieces from different heights until they are broken. The results of this test checked closely with different sizes of test pieces. The following results were obtained on a number of porcelains.

	A	B	C	D	E	F	G	H
1—Insulator body G.....	4000	..	481	590	0.90	98	...	2.4
2—Insulator body H.....	5000	261	500	540	0.95	105	5630	3.3
3—Table ware.....	..	..	..	640	1.36	112	..	..
4—Chemical porcelain.....	..	..	500	410	1.23	117	5930	..
5—Hermisdorfer hard porcelain.....	4780	..	..	490	..	..	5050	..
6—Hard porcelain No. 6292 (Amer.) ..	..	..	..	520	0.08	..	..	..
7—Seger porcelain, No. 6833.....	..	..	430	..	1.00	69	5340	..
8—Special body No. 6412.....	..	..	..	980	2.40	146	..	1.7
9—Special body No. 6048.....	..	..	..	..	1.61	..	6680	..
10—Glass pot body.....	..	..	..	..	0.34	8	..	..
11—Refract. body.....	..	..	..	..	0.33	7	..	..

$A$  = compression strength in kg. per sq. cm.,  $B$  = tensile strength in kg. per sq. cm.,  $C$  = torsion strength in kg. per sq. cm.,  $D$  = cross-breaking strength in kg. per sq. cm.,  $E$  = impact cross-breaking strength, cm. in kg. per sq. cm.,  $F$  = impact compression strength, cm. in kg. per sq. cm.,  $G$  = velocity of transmission in m. per sec., and  $H$  = loss in vol. from sand blasting test. One test is not sufficient to measure the strength of porcelains. Many porcelains which stand up well in one test fail in another. This is true of the Am. porcelain 6292 which stands up well in cross-breaking strength but fails in the impact test. Bodies  $G$  and  $H$  also stand up well in cross-breaking strength but fail to show a high resistance to impact.

H. G. SCHURCHT

**The manufacture of pressed porcelain.** ERICH RUTH. *Keram. Rundschau* 29, 33-9(1921).—Porcelain elec. insulators are either turned or pressed. The high tensile insulators are usually turned. For pressed insulators cheaper materials may be used. The bodies after being dried are mixed with pressing oil and water and after storing are pressed. Many pieces may be made by automatic machinery.

H. G. SCHURCHT

**The Chicago method of firing brick.** F. H. LAMBERT. *Clayworker* 75, 244-8 (1921).—The firing of scove kilns is described.

H. G. SCHURCHT

**Drying brick and tile.** J. L. BUCKLEY. *Clayworker* 75, 237-8(1921).—In the Procter system of drying the air blows across the drier. Temp., air circulation and humidity can be controlled. Glass pots, high tension insulators, etc., which require a long time for drying, can be successfully dried in humidity driers in a comparatively short time.

H. G. SCHURCHT

**Comparative cost of steam and electric power in the brick industry.** C. CORDES. *Clayworker* 75, 251-2(1921).—Elec. power is shown to be cheaper.

H. G. S.

**A new electric testing furnace.** ANON. *Keram. Rundschau* 29, 69-70(1921).—A Cressistance furnace having a heating chamber 11.5 cm. in diam. and capable of holding a crucible  $0.5 \times 15$  cm. is described. It has a movable bottom. It may be used for the continuous melting of fritts, glasses, etc. The max. temp. obtainable is about cone 28.

H. G. SCHURCHT

**Possibilities for research and development in the field of refractories.** HOMER F. STALEY. *Chem. Met. Eng.* 23, 1167-71(1920).—Firebrick represent 50% in value of the total refractories produced in the U. S. S. suggests further study of sillimanite and SiC refractories, and of the use of  $\text{SiO}_2$  brick in car-tunnel kilns. More common use of insulating brick would change the whole status of the use of refractories.

DONALD E. SHARP

**Abrasives and grinding wheels bonded with ceramic materials.** KARL HECHT. *Keram. Rundschau* 28, 511-2, 521(1920).—A mixt. of clay and a feldspar fritt is used as a bond. The bond should be soft for grinding hard steel but hard for grinding cast Fe since it is desirable to have the abrasive particles remain intact until they are worn smooth. By a patented process the abrasive material is sepd. from old grinding wheels by grinding, and heating under pressure with an alk. soln. which causes the bond to swell and finally the bond is removed by treatment with dil. acids.

H. G. SCHURCHT

Furnaces [drying clays, dehydrating gypsum, etc.] (BRIT. PAT. 152,602) 1.

**Glass.** E. C. SULLIVAN and W. C. TAYLOR. U. S. 1,369,988, Mar. 1. A glass adapted for manuf. of elec. lamp bulbs is formed of  $\text{SiO}_2$  62-79.4,  $\text{Na}_2\text{O}$  16-23,  $\text{MgO}$  1.6-15,  $\text{CaO}$  0-8.8 and  $\text{ZnO}$  0-3.1 parts.

**Pottery.** A. P. MORRIS. Brit. 155,322, Aug. 15, 1919. Potteryware which has been blackened during firing by deposition of C is ornamented by removing parts of the C deposit by oxidation, thus revealing the natural color of the clay. In the preferred process a paste of clay with an oxidizing agent, e. g.,  $\text{KClO}_3$ , is applied in a pattern to

the blackened surface, and the article is heated to a temp. sufficient to release the O but below that at which the clay is fired. By suitable selection of the clay used in making the ware different colorings may be produced in different parts of the figuring. Cf. C. A. 15, 740.

**Electrical insulating composition.** H. H. BUCKMAN and G. A. PRITCHARD. U. S. 1,370,276, Mar. 1. A ceramic elec. insulating material is formed of a porcelain-like compn. in the manuf. of which zircon or Zr silicate is partly or wholly substituted for china clay.

## 20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILEY

**Pouring and pressure tests of concrete.** W. A. SLATER and A. T. GOLDBECK. Bur. Standards, *Tech. Papers*, No. 175(1920).—The paper is divided into 2 parts: (1) Pouring, consistency, and compressive-strength tests of concrete in cylinders and slabs and (2) measurements of pressure of concrete against forms during pouring. The paper presents results of 3 minor investigations carried out at the request of the concrete ship section of the Emergency Fleet Corporation. With gravel aggregate, a smooth dense surface suitable for the shells of concrete ships was obtained. The max. pressure against the forms during pouring was equiv. to that of the liquid weighing about 124 lbs. per cu. ft. J. C. WYRR

**Relative heat conductivities of some insulating and building materials.** JAMES J. LICHTIN. Verona Chem. Co., Newark, N. J. *Chem. Met. Eng.* 24, 388(1921).—Heat was supplied inside a box made of the material tested, and the resulting inside-outside temp. differences were observed. It is pointed out that a little thermal resistance of air is included. Some results differ 10% or 20% from those of Dickinson and Van Dusen. For temps. from 70° to 150° F., the c. g. s. cond. was: concrete (1 cement, 2 sand) 0.000727, gypsum board 0.000349, "Porete" (reinforced) 0.000324, "Virginia" pine 0.000297, "Air cell" 0.000138, cork board 0.000144. Porete is a porous construction of cement and sand. W. P. W.

**Zinc fluoride as preservative for wooden telegraph poles and cross bars.** ROBERT NOWORNY. *Oesterr. Chem. Zig.* 23, 136-8(1920).—Actual field tests extending over a period of 8 years indicate that  $ZnF_2$  is a more effective preservative for telegraph poles than is  $CuSO_4$ . The impregnating soln. was prep'd. by mixing 1.75%  $ZnCl_2$  soln. with a soln. containing the same wt. of NaF. Pine poles were treated (with 150-180 kg. soln. per cu. m. of wood). The  $ZnF_2$  solns. as well as the basic fluoride which is formed in the wood are powerful fungicides. More than 15,000 poles were treated in this way and the total loss (through deterioration, etc.) during 8 years of exposure approximated 6%. A similar series of exposure tests, carried out by Boucherie (ref. no. given) under similar climatic conditions, with  $CuSO_4$  as a preservative, showed a loss of 34.5% during the same time period. N. discusses the difficulties and limitations of the  $ZnCl_2$ -NaF impregnation methods and recent modification of the  $ZnF_2$ . Premature  $ZnF_2$  formation must be prevented and poles should be air-dried prior to their erection. L. E. WISS

Specifications for asphalt for use in damp-proofing and waterproofing (ANON.) 22.  
Specifications for coal-tar pitch for use in damp-proofing and waterproofing (ANON.) 21.  
Potash shales of Illinois (PARR, AUSTIN) 15.

**Concrete.** L. H. DYER. U. S. 1,369,794, Mar. 1. Hollow bodies of Fe or steel or other metal are used as aggregate in concrete for producing a light material.



**Treating cement, etc., with liquids.** W. PATTISON. Brit. 155,883, Sept. 11, 1919. An app. for hardening, curing, coloring, etc., sheets of asbestos cement or the like by treatment with a number of liquids in succession consists of a number of chambers provided with heating coils and connected to a series of vats for containing the treating liquids by a system of pipes, provided with pumps and cocks so that any one of the liquids can be supplied to or withdrawn from any one or any number of the chambers as required. The chambers are provided with steam- and liquid-tight doors, and rails allow the sheets to be introduced into the chambers easily. Means may be provided for siphoning liquid from one chamber to another. The sheets may be first heated and treated with dry air, then soaked in  $H_2O$ , then treated with acid to neutralize alkali, and then with a coloring liquid.

**Quickly solidifying cement.** R. OGAWA. Japan 36,334, May 7, 1920. Clay, containing above 60%  $SiO_2$ , above 20%  $Al_2O_3$  and below 10%  $Fe_2O_3$  is mixed with lime in the ratio  $CaO/(SiO_2 + Al_2O_3 + Fe_2O_3) > 2$  and the mixt. is burned at  $1500-1550^\circ$  to a clinker, and then mixed with 4% mixt. of natural gypsum and plaster of Paris in the ratio 3:1, crushed and sieved. The product solidifies completely within 3 hrs.

**Magnesia cement.** M. ÔURA. Japan 35,971, March 12, 1920. The cement is prepd. by mixing together (1) and (2). (1) Mixt. of 60 parts  $MgO$  and 10 parts of fibrous substance of vegetable or animal origin, e. g., chaff or powdered cork. (2) Ten-parts of soln. of powdered *Hydrome rivieri* and *Gloiopeltis furcata* are mixed with 15 parts asbestos or kieselsguhr, dried and powdered and mixed with the proper pigment and 5 parts of burnt alum.

**Artificial stone.** R. SHINYA. Japan 36,376, May 13, 1920. The stone is prepd. by thoroughly mixing 1.8 l. magnesite, 1.08 l.  $ZnO$  and 0.72 l. glass powder with 1.44 l.  $MgCl_2$  soln. ( $30^\circ B_6$ ).

**Roofing material.** K. TAGAWA. Japan 36,381, May 15, 1920. Asphalt 10 is melted with vegetable wax 2 and Al soap 1 under agitation (I). Stearin pitch 2 is treated with S 0.1-0.2 and mixed with nitrated oil 1, which is added to (I) with finely powdered leather under heating and is then painted on cloth or stout paper and dried.

**Roofing and wall-covering composition.** T. H. BROWN AND H. BROWN. U. S. 1,369,911, Mar. 1. The compn. is formed of ashes and fine cinders 50, asphalt 25 and waste broom straw 25%.

**Tile made of paper.** Y. SAKAKIBARA. Japan 35,965, Mar. 11, 1920. Paper manufd. from strong fiber containing tannin, is soaked in a soln. of  $(NH_4)_2SO_4$  30,  $ZnCl_2$  6, Na silicate 10, boric acid 10, and  $H_2O$  400, and dried, then painted with a mixt. of asphalt 30, coal tar 40, drying oil 10, graphite powder 10, and asbestos powder 10, and finally with graphite powder. It is then rolled and dried.

**"Wood substitute."** G. D. ROSE. U. S. 1,370,155, Mar. 1. A material adapted for use instead of wood in making frames or vehicle bodies is formed of coir fiber impregnated with rubber, compressed and vulcanized.

## 21--FUELS, GAS, TAR AND COKE

A. C. FIELDNER

**Fuel Research Board's examination of the Simmance total-heat recording calorimeter.** ANON. *Tech. Paper* No 1; *Gas World* 74, 231(1921); *Gas J.* 153, 739-40 (1921).—Continuous tests for 7 months were made. The variations of the recorder seldom exceeded 2% and it responded well to rapid and extreme changes of density and calorific value in the gas. J. L. WILEY

**The origin and chemical structure of coal.** FRANZ FISCHER AND HANS SCHRADER. *Mülheim-Ruhr. Brennstoff Chem.* 2, 37-45(1921).—The hypotheses of previous in-

investigators as to the origin of humic acids, peat and coal have been based largely on the assumption of a degradation of cellulose, phenol formation on distn. being dependent on the presence of the furan grouping. F. and S. picture the following relationships and processes: (1) Lignin has an aromatic structure, with acetyl and methoxy groups; (2) cellulose is largely destroyed by bacterial activity in the early stages of peat formation, with the formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ; (3) the methoxyl content of peat must therefore increase and the portion sol. in concd.  $\text{HCl}$  decrease with increasing age; (4) the methoxyl content must eventually decrease owing to sapon., reduction, or replacement by  $\text{OH}$ , but in any case a phenol results, which is taken to be identical with humic acid; (5) oxidation or polymerization of humic acid forms the alkali-insol. humin; (6) further splitting off of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , and perhaps  $\text{CH}_4$ , at ordinary temp. leads to lignite and coal. The whole series thus is assumed to perpetuate the aromatic structure of lignin. The first point is supported by the work of Klason (*C. A.* 11, 2482), Hönig and Fuchs (*C. A.* 14, 1675) and Melander (*C. A.* 14, 838). As to the second point, Stutzer has shown (*Glückauf*, 56, 686) that bacterial action continues even in the deeper peat layers. Rose and Lisse showed that in decaying wood the lignin was more resistant than the cellulose (*C. A.* 11, 1674). Work done by the authors, with Friedrich, supported points (3) and (4), a young peat bed showing increased methoxyl content with increasing depth, an old black-peat bed, on the other hand, a decrease from 2.97% to 1.66% with increasing depth, the portion insol. in concd.  $\text{HCl}$ , however, constantly increasing in the whole series. Digestion of lignin (from wood with concd.  $\text{HCl}$ ) with 4 *N*  $\text{KOH}$  gave humic acid at  $200^\circ$  and an insol. humin and  $\text{MeOH}$  at  $300^\circ$ , while cellulose under the same conditions gave neither. Various workers have shown that natural and artificial (from sugar) humic acids, and cellulose give protocatechuic acid when fused with  $\text{KOH}$ ; but the yield from the natural acids is higher than that from the other two. F.'s pressure oxidation of cellulose at  $200^\circ$  gave fatty acids and  $(\text{COOH})_2$ , while lignin gave a deep-brown soln. containing humic acids, which cleared up at  $400^\circ$  with the formation of  $\text{BzOH}$  and isophthalic acid. When various types of coal were similarly treated, aromatic acids were formed, but no furan derivs. These same acids were found in the oxidation products of  $500^\circ$  coke and even in the trace of acid products from  $1000^\circ$  coke. Many investigators have shown that mellitic acid is a const. oxidation product of coals and ignited charcoal (e. g. Meyer and Steiner got a yield of 40% of mellitic acid from charcoal, *C. A.* 8, 3032). The fact that cellulose yields  $\text{PhOH}$  almost exclusively on distn., while coal yields principally the higher homologs, seems to be further indication of the absence of cellulose derivs. The high wax content of certain peats and lignites is explicable as a result of the disappearance of cellulose; most mosses contain but little lignin, so that removal of the principal constituent, cellulose, results in a magnification of the small original wax content.

W. B. V.

**Sulfur in coal and coke.** ALFRED R. POWELL. *Proc. Eng. Soc. Western Penn.* 36, 611-40(1920); cf. *C. A.* 14, 619, 3145; 15, 306, 742.

J. I. W.

**Analysis of Iowa coals.** GEORGE S. RICE, A. C. FIELDNER AND F. D. OSGOOD. *Bur. Mines, Tech. Paper* 269, 28 pp.(1921).

E. H.

**The inorganic constituents of coal, with special reference to Lancashire seams.** F. S. SINNAT, A. GROUNDS AND F. BAYLAY. *J. Soc. Chem. Ind.* 40, 1-47(1921).—The purpose of the investigation reported was (1) to det. the relationship between the compn. of the white partings or ankerites (substituted  $\text{CaCO}_3$  or dolomitized siderite) of the low-ash coal of the Lancashire seams and that of the ash produced on incineration, (2) to trace the source of the  $\text{CO}_2$  evolved on treatment of the coal with acids, and (3) to det. the form in which  $\text{Fe}$  exists in the coal substance. Analysis of ankerite and ash gave widely differing results, showing lack of close relationship. It was found, furthermore, that the  $\text{CO}_2$  evolved with acid treatment of the coal was in excess of that

equivalent to the basic constituents, indicating other sources of  $\text{CO}_2$  than the ankerite, and finally that Fe occurred almost entirely in the ferrous state. For a report on some org. constituents of these coals see *C. A.* 14, 3516.

H. L. OLIN

**Cannel coal in southern Utah.** C. A. ALLEN. *Bur. Mines, Repts. of Investigations* 1921, No. 2221, 3 pp.—Cannel coal of the following proximate compn. occurs in a difficultly accessible region of southern Utah: loss on air drying, 4.5; on air dry basis, moisture 11.77; volatile, 43.89; fixed C, 29.32; ash, 15.02; S, 1.38. Microscopical examn. shows it to be a high-grade cannel. Tests made at the Salt Lake station gave the following results: gallons of oil per ton, 68.8; sp. gr. of oil, 0.8045; setting point, 36°; ash in coal, 22.2%; N, 1.3%. See also description in *Bull.* 341, U. S. Geol. Survey under the title of Colob Coal Field.

H. L. OLIN

**Tentative method for determination of fusibility of coal ash.** ANON. *Proc. Am. Soc. Testing Materials* 20, 1, 796-803 (1920).—This method has received serial designation p22-19r. A No. 3 melter's furnace of the Am. Gás Furnace Co., or its equiv., shall be used, with natural or artificial gas under pressure of 3 lbs. per sq. in. The furnace is modified by introducing a 2-in. hole for observation, and a 1-in. hole at right angles to the first for a thermocouple, the holes being on the same horizontal plane. From 50 to 100 g. of 60-mesh coal are ashed in a 6-in. fireclay dish in a muffle furnace at 800-900°, and 5-10 g. ground in an agate mortar to 200-mesh, then ignited in  $\text{SiO}_2$  or porcelain capsules for 2 hrs. in O at 800-850°. The ignited mass is moistened with 10% dextrin soln., worked till plastic, and molded in a brass mold into pyramids 0.75 in. high, with bases consisting of equilateral triangles 0.25 in. on a side. When dry, the test pyramids are mounted in a vertical position in a refractory base made of equal parts of kaolin and calcined  $\text{Al}_2\text{O}_3$ , about 5 pieces in one base. The whole is then dried on a hot plate, ignited to redness 30 min. in an open muffle, then placed on the lid of a covered No. E Denver fireclay hard-burned crucible, which is placed inside a No. K crucible, provided with 2 holes registering with the holes in the furnace. The outside crucible is covered, and a fused  $\text{SiO}_2$  or porcelain observation tube inserted through the furnace and crucible, carrying at its outer end a brass sleeve with a thin glass window to prevent the escape of gases. The thermocouple is inserted, with its end on the test piece, and also through the same hole a 0.25-in. porcelain tube, for blowing air against the pyramids momentarily, to render them visible when hot. The gas is allowed to burn 10 min. before covering the furnace; then the gas flow is increased until a yellow reducing flame is maintained at least 6 in. above the opening in the furnace cover. After 800° is reached, a rise of 5-10° a min. is maintained. The softening temp. is the temp. at which the pyramids fuse to spherical lumps. A difference of 30° is allowed in duplicate detns. by the same analyst, and 50° in detns. by different analysts. The thermocouple should be frequently checked against Au (m. 1063°) or Ni (m. 1452°), and should be standardized over its whole range by a properly equipped lab., such as the Bureau of Standards.

M. R. SCHMIDT

**The calculation of the heat losses in boiler flue gases.** CH. DE LA CONDAMINE. *Industrie chimique* 8, 89-92 (1921).—The formula  $P = 0.68 \frac{(t-t')}{A}$ , where  $P$  is

the loss per 100 cal. of heat available in the coal,  $t$  the temp. of the flue gases,  $t'$  the atm. temp., and  $A$  the %  $\text{CO}_2$  by vol., is shown to give fairly accurate results when  $t$  is low,  $A$  is fairly high, and the unburned coal in the ashes is negligible. In all other cases it should not be used. The formula does not take into consideration the moisture in the coal and the combustible gases in the flue gases, nor does it give the loss due to excess air. It is better and safer to make a proper calcn. of the losses for each case being studied, which is neither long nor difficult with the aid of proper tables.

A. P.-C.

**Liquid fuel in peace and war.** FREDERICK BLACK. *Pet. Times* 5, 181-2(1921).—An address.

R. L. SIBLEY

**The carburation of alcohol.** A. W. SCARRATT. *J. Soc. Autom. Eng.* 8, 328-30 (1921).—Expts. showed that more heat is needed for good operation on alc. than is required in using kerosene as a fuel for tractor engines but the power developed is equal to that given by a good grade of kerosene. The most satisfactory results were obtained by using a compression of 110 lbs., although very liberal provision for heating the fuel charge to at least 100° F. must be made. This may be done by utilizing the entire exhaust heat.

R. L. SIBLEY

**The behavior of certain coals in low-temperature distillation.** FRITZ FORSTER. *Dresden. Brennstoff Chem.* 2, 33-7, 65-73(1921).—Six representative gas-coals from Oberhohendorf, Bockwa and Zwickau, in Saxony, were investigated for behavior in low temp. distn. The compns. of the 6 varieties did not vary widely, averaging as follows: ash, 7%; moisture, 9.5%; C, 70.5%; H, 4.0%; N, 1.65%; S, 1.5%; calorific value (dry, ash-free), 8800 cal. per g. Samples weighing 3 kg. were distd. in a rotating furnace similar to the one described by Fischer and Gluud; superheated steam was passed in at the rate of 1.7 kg. per hr., which is proportionately 3 to 5 times as much as was used by F. and G. Gas evolution began at about 350°; the temp. was raised rapidly to 400-420° and when gas evolution nearly ceased, to 500-20°. About 1½-2 hrs. elapsed between the first gas evolution and the final rapid subsidence at 500°. The nature and quantity of the products were similar to those previously reported for other gas-coals, the tar yield and percentage of non-viscous and lubricating oils in the tar being almost identical with results F. and G. obtained with a Rhenish coal. The gases accompanying the first tar formation, up to about 420°, possessed the high calorific value of 9000-10,000 calories per liter. The gases in this stage of the distn. were rich in H<sub>2</sub>S, in some cases contg. 7 to 9%. Between 420° and 500° the yield of tar decreased considerably and the volume of gases increased.

W. B. V.

**The variation in tar recovery in the distillation of lignite.** FRANZ FISCHER, WILH. SCHNEIDER AND ALBERT SCHELLENBERG. *Mülheim. Brennstoff Chem.* 2, 52-8(1921).—Lignite from various German sources was tested for tar production (cf. C. A. 14, 3149) in (1) moist condition as mined, (2) air-dried, (3) dried at 105° in a CO<sub>2</sub> stream, and (4) dried at 105° in the air. In cases (2) and (3) the tar production was about 25% less than in case (1), apparently owing to auto-oxidation, while in case (4), the yield was about 45% less than in case (1), because of oxidation by the air during drying.

W. B. V.

**The montan wax content of lignite low-temperature tars and low-temperature paraffin.** WILHELM SCHNEIDER AND OTTO JANTSCH. *Brennstoff Chem.* 2, 60-1(1921).—No method of distn. of tars or crude montan wax has been discovered which results in satisfactory yields of purified wax, extn. with benzene or benzene-alc. being the best present practice.

W. B. V.

**The pressure-oxidation of lignite tar-oil.** FRANZ FISCHER AND WILHELM SCHNEIDER. *Brennstoff Chem.* 2, 76(1921); cf. C. A. 15, 801, 743.

W. B. V.

**The use of phenol-containing tar fractions as a fuel in internal-combustion engines.** HANS SCHRADER. *Brennstoff Chem.* 2, 77(1921).—A tar oil b. 175-250° containing about 45% phenols has been used without trouble in an oil-burning engine, by starting with a light hydrocarbon and keeping the cooling water up to 100°.

W. B. V.

**The corrosion of metals by tar phenols.** FRANZ FISCHER. *Brennstoff Chem.* 2, 77-8(1921); cf. Ehrhardt and Pfeiderer, C. A. 15, 942.—The losses in wt. of metals exposed to tar oil, reported by E. and P., may not have been due to the phenol content of the oil, but to S compds., etc.

W. B. V.

Tentative specifications for coal tar pitch for use in damp-proofing and water-proofing. ANON. *Proc. Am. Soc. Testing Materials* 20, 1, 721-4 (1920).—The serial designation is D42-17T. The m. p. by the half-inch cube method, in a water bath, is 49–60° ± 2.5°. The penetration at 25° under 100 g. load for 5 sec. is 20–120. Ductility at 25° is not less than 40 cm. on 1 sq. cm. cross section. Loss on heating at 163° for 5 hrs. is not greater than 9% for 49–54.5° m. p. and not more than 7% for 54.5–60° m. p.  $d_{25}^{25}$  1.24–1.34;  $d_{80}^{80}$  of distillate from 100 g. up to 355° (vapor temp.) is not less than 1.06. From 65 to 85% is sol. in hot  $C_7H_8-C_8H_8$ . The ash on a 1 g. sample is not more than 1%.

M. R. SCHMIDT

The coking plant of the Rhenish steel works in Duisburg-Meiderich and the use of silica brick for coke ovens. J. ENGENAUER. *Stahl u. Eisen* 40, 1326–35 (1920).

CARLE R. HAYWARD

Tests of miners' flame safety lamps in gaseous, coal-dust-laden atmospheres (ILSLEY, HOOKER) 1. Origin of natural fuels (RICAUD) 8. German fossil resin (PATZSCHKE) 26. Ammonia (GER. PAT. 321,661) 18.

BEARD, JAMES T.: *Mine Gases and Ventilation*. 2nd. ed. revized. New York and London: McGraw-Hill Book Co., Inc. 433 pp. \$4.00. For review see *Proc. Am. Soc. Civil Eng.* 46, 880 (1920).

Artificial fuel. W. BROADBRIDGE. *Brit.* 155,875, Aug. 26, 1919. Coal briquets are made from coal concentrates, which may be obtained by treating impure coal, coal dumps, etc., by froth-flotation processes, by obtaining a suspension of the powdered concentrates in  $H_2O$  and subjecting to agitation with a liquefied binding agent, whereby the coal particles are coated with binding medium and flocculated so as to be readily separable from the  $H_2O$ . A flocculating agt., such as slaked  $CaO$ , or  $Na_2SiO_3$ , may be added to the pulp of coal concentrates in  $H_2O$  and may act also as an auxiliary binding agent. The liquefied binding agent may be melted pitch, with or without tar, resin, etc. When the concentrates are obtained by froth-flotation processes, a liquid agent which contains or yields both a frothing agent and a binding medium may be used. The agitation of the coal-water pulp with the binding agent is carried out with a greater or less degree of aëration. The concn. of the coal by the froth-flotation process and the coating of the coal particles with the binding medium may be combined into a single operation, which may be continuous. The amt. of pitch used may be 7% of the wt. of the coal reckoned dry, or 5% of pitch may be used together with cresol and kerosene oil. Cf. 26,295, 1902, and 7803, 1905.

Material for purifying gas. J. E. HUTCHINSON. U. S. 1,370,494, Mar. 1. A material adapted for removing S compds. from gas is formed of porous plaster compn. or similar material carrying a purifying agent such as hydrated Fe oxide upon its surface and within its pores.

Gas-purifying material. J. E. HUTCHINSON. U. S. 1,370,495, Mar. 1. A porous concrete formed of cement, silica and hydrated Fe oxide is used for purifying gas.

Coking oven. O. PIETRE. U. S. 1,370,481, Mar. 1.

Retorts. G. B. ELLIS. *Brit.* 154,819, Jan. 29, 1920. In a vertical retort having an outer shell formed with annular heating flues, and an inner shell formed of frusto-conical rings through which the gas is withdrawn, the lining of the outer shell is formed of argillaceous material such as fire-clay bricks at the upper part, and of ribbed, siliceous bricks at the lower part. The vapors and gases escape through telescopic pipes, the ends of which are adjusted to enable moisture and gas to be withdrawn separately. Steam is injected through a pipe located within one of the lower rings, in order to in-

crease the production of  $\text{NH}_3$  which collects below a diaphragm and escapes through a pipe. The temp. may be determined by thermostats which are inserted in holes, leading, resp., to the flues and the charge; gas is supplied through pipes to increase the temp. at any level, and air inlets with sliding bricks enable the temp. to be reduced. The carbonized product is discharged from a chute through a rotating gate.

**Internal-combustion engines.** J. P. REYNHOUT. Brit. 155,100, Nov. 18, 1919. Consists in coating sparking-terminals with an alloy of Ag and Au by immersion in the molten alloy, or preferably by galvanic action.

## 22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

**Recoverable oil in by-product sands and outcrops.** A. R. ELLIOTT. U. S. Bur. of Mines, *Repts. of Investigations*, Serial No. 2182, Nov. 1920.—A survey of the oil districts of California to ascertain if the visible masses of wasted oil-bearing sands would be a profitable source of supply. The possible sources are: (1) Oil left in the sand that is produced with the oil; (2) oil that seeps into the ground through waste in production; and (3) oil-bearing outcrops and asphalt beds that occur in certain regions of the state. It is estd. that 2,359,000 barrels of oil could be obtained from the sand piles about producing wells and from the outcroppings in the vicinity of the fields. The amt. of sand produced varies from 20 to 60% of the total production of the wells. The method of analysis of the sand was to heat in a closed retort and condense the vapors. The amt. of oil recovered in this way varied from 11 to 62 gals. to the ton. Tabular data are given under the following titles: Analysis of sands from wells and outcrops in the Calif. fields; estimates of oil content in sands and outcrops; and analyses of asphalts in Calif.

F. W. PADGETT

**Oil fields of Central Montana.** FRANK REEVES. U. S. Geol. Surv. *Oil and Gas* J. 19, 42, 68–72 (1921).—Preliminary account of an area of about 800 sq. mi. in Central Montana. The area includes the greater part of a plunging geanticline, along the northern and southern flanks of which there are 2 pronounced anticlinal folds and along the axes of these folds there are several oval domes. There are several small producing wells in this field and 3 paying wells. The oil is a paraffin base containing but little S. It has a sp. gr. of 49.7° Bé. and has a gasoline content approx. twice that of the av. Mid-Cont. oil.

R. L. SIBLEY

**The possibility of oil discovery on the mainland of Australia.** WM. CLARKSON. *Pet. Times* 5, 309–11 (1921).—Extraordinarily rich oil shale exists in almost unlimited quantities in Australia, in Tasmania and in N. S. Wales. Several wells have been sunk and in some cases gas has been obtained, but no oil thus far. In one well the gas contd. 150 gal. of gasoline per million cu. ft. of gas.

R. L. SIBLEY

**The crude oils of Borneo.** JAMES KELWAY. *Pet. Times* 5, 337–9 (1921).—The crude petroleum which are found in large quantities in Borneo show a considerable variation in type. There are 3 important producing areas which differ in respect to the types of oil they yield. Crudes from the Koetei field have a high aromatic content and are particularly rich in unsatd. hydrocarbons, some containing as high as 86% unsatd. compds. in the benzene and kerosene fractions. A sample of benzene from this field having a d. of 0.783 and a final b. p. of 165° contained 40% of aromatic hydrocarbons made up of 7%  $\text{C}_{10}\text{H}_8$ , 14%  $\text{C}_7\text{H}_8$ , 15%  $\text{C}_6\text{H}_4(\text{CH}_3)_2$ , and 4% higher hydrocarbons. These can be sepd. by means of fractional distn. in steam stills fitted with Heckmann columns of normal type. Crudes from the Tarakan fields are used almost entirely as fuel oils and contain no gasoline fraction; but 0.8% distg. up to 220°. They are all of the asphalt base type. The crudes from the Miri field yield about 20%

of a benzine low in volatile fractions and 30% of kerosene and contain no asphalt. The geological structures of these fields tend to confirm Mabery's theory that coal is an intermediate state of decompn. between vegetable substances and petroleum.

R. L. SIBLEY

**The chemistry of Egyptian petroleum.** I. W. A. GUTHRIE. *Pet. Times* 5, 327-8 (1921).—Fractional distn. of oil from various wells showed that the oil is decidedly poor in the lighter products (5 to 7%) while the kerosene content is about 15%. The residue is very thick. The crude oil (Hurghada) is a brownish black oil contg. about 2.43% S, 10.57% asphalt, 7.73% paraffin wax having a m. p. of 117° F. The oil is undoubtedly a mixt. of paraffin-base and asphalt-base petroleums rich in S and would be a difficult one to refine. The lighter fractions from most specimens are rich in olefin hydrocarbons and contain appreciable amts. of aromatic hydrocarbons. The residue "mazut," remaining after the kerosene and lighter spirit fractions are removed, contains so much asphalt and paraffin wax that they are suspended as solids and in cold weather can scarcely be forced through a pipe line. The "mazut" (kerosene-free) has a viscosity (Redwood) at 100° F. of 6878 sec., but if 7% kerosene is present, the viscosity is 3159 sec., while if all the kerosene (14%) is present, the viscosity is 926 sec. The "mazut" is unsuitable for use in internal-combustion engines because of the asphalt content and the presence of salt, together with traces of sand, gypsum and clay. In order to improve the products, the crude was refined as follows: a distn. was made to coke and 2 fractions were collected, (1) the petroleum spirit and (2) all the higher boiling fractions. The second fraction was redistd. after chem. treatment by means of superheated steam and the following fractions were condensed: kerosene, intermediate fuel oil and paraffin fractions. The last of these distillates was cooled and the wax extd. in the usual way. The filtrate was "concd." by superheated steam to produce heavy lubricating oil and more fuel oil. The general results are as follows: petroleum spirit 7.7%, kerosene 14.2%, fuel oil (thin) 21.6%, lubricating oils 24.5%, crude paraffin 6%, coke 12.2%, loss 13.8%. The mixed lubricating oils could be marketed as a thin machine oil without further treatment. II. *Ibid* 362-3 (1921).—Another method of refining Egyptian oils is to crack the "mazut" in a special still. By this process there was obtained 4.5% light petroleum spirit, 2.7% heavy petroleum spirit, 16.5% kerosene distillate, 20.2% heavy distillate, 25.6% Diesel fuel oil, 23.1% coke, and 7.4% loss. The fuel oil was too good in quality for use in firing boiler furnaces, but a satisfactory product was obtained by mixing 4 parts of "mazut" to 1 of fuel oil for summer use and 1 to 2 parts for winter use. Many of the crudes are obtained as very refractory emulsions, and ordinary methods of breaking emulsions, such as centrifuging, heating at 100° and the action of air currents, were unsatisfactory. An electrical method gave better results and it was shown that an oil containing 10% H<sub>2</sub>O and 2% salt was reduced to 1.04% H<sub>2</sub>O and 0.19% salt after 4.5 hrs. treatment at 60° with a high tension intermittent unidirectional current of 12,500 volts.

R. L. SIBLEY

**Evaporation losses of petroleum.** J. H. WIGGIN. U. S. Bur. Mines. *Oil and Gas J.* 19, No. 44, 76-80 (1921); cf. *C. A.* 14, 2547.—Evapn. tests carried out under identical conditions in the lab. indicated that gasoline derived from light crude will evap.  $\frac{1}{2}$  as rapidly when still in the crude state as when it has been distd. and exposed in the pure state. However, the blending of a gasoline with a heavy, viscous, high-flash oil will decrease its rate of evapn., in some cases as much as  $\frac{2}{3}$ .

R. L. SIBLEY

**Vapor pressure of gasoline and gravity.** J. H. WIGGIN. U. S. Bur. Mines. *Oil and Gas J.* 19, No. 42, 56-8 (1921).—The % of gasoline necessary for satn. of air varies as the sp. gr. (Bé.) of the gasoline varies. In the case of breathing of tanks, the % of gasoline vapor in the mixt. forced from the tank has direct bearing on the volumetric loss due to evapn. Convection currents are readily set up in steel tanks unprotected from the

sun's rays. Calcn. shows that a 1% evapn. of light gasoline from crude oil will have approx. the same effect on the sp. gr. of the crude as a change of 4° to 8° F. in temp. After 44 days storage during the summer, the sp. gr. of oil in a 500-bbl. tank (steel jacketed) dropped from 37.3° Bé. to 36.5°, while in an unprotected steel tank of the same capacity, the decrease was from 36.8° to 34.5°. The drop in an unprotected 250-bbl. tank was even greater, being from 37.3° to 33.3° Bé. Results of over 200 distn. tests checked with actual field results showed that the heavier fractions evapd. practically not at all as long as there remained some fractions that were considerably more volatile. Thus, after 44 days storage in the 250-bbl. unprotected steel tank, portions boiling at about 280° F. were evaporating while from the 500-bbl. steel-jacketed tank the fraction from 160° to 180° F. was being lost. This means that the former was losing portions having an av. sp. gr. of 67° Bé., while the latter was losing gasoline of 81° Bé.

R. L. SIBLEY

**Use of the MacMichael viscosimeter in testing petroleum products.** W. H. HERSCHEL and E. W. DEAN. U. S. Bur. of Mines, *Repts. of Investigations*, Serial No. 2201, Jan. 1921.—The object is to outline in a simple manner the principles involved in the calibration and use of the MacMichael viscosimeter and to describe a procedure that has proved satisfactory in the respective labs. of the authors. The advantages and limitations, description and calibration of instrument, are considered (see also Herschel, *C. A.* 14, 1065, 2567). The app. has the advantage of rapid detn. and will measure the viscosity of products that are not entirely homogeneous, such as emulsified products. It is also of value in distinguishing true liquids from plastic solids, but is hardly a satisfactory substitute for the familiar efflux-type instruments for general use. The instrument should be calibrated by means of oils of known viscosity. The most convenient method of detg. the calibration factor is to adjust the speed of the cup so that the deflection is some simple multiple or fraction of the abs. viscosity of the oil used for calibration. This involves the use of the equation  $V_a = cM$ , where  $V_a$  = the abs. viscosity,  $M$  = the deflection, and  $c$  = const. that is characteristic of conditions of operation and adjustment. This is permissible if the viscosity of the oil used is not lower than 1 poise, or if it is lower than 1 poise, but the deflection measured is in excess of 100°  $M$ . Calibrations should be made before and after each series of tests on unknowns. MacMichael readings are translated into abs. viscosities and the latter into Saybolt equivs. as follows: Multiply the MacMichael deflection by the figure or fraction detd. as the calibration const. to get the abs. viscosity  $V_a$ . Divide  $V_a$  by the d. of the oil at the temp. in question, to get the kinematic viscosity  $V_k$ . If  $V_k$  is less than 0.652 find the Saybolt Universal equiv. by reference to the table of kinematic viscosities equiv. to Saybolt Universal viscosities. If  $V_k$  is greater than 0.652 find the Saybolt Universal equiv. by multiplying by the factor 454.5.

F. W. PADGETT

**Petrol-alcohol chemical discovery.** CARLETON ELLIS. *Petroleum Mag.* 10, 40-1 (1921).—The process as developed by E. is based upon the following reactions: (a) the formation of olefins such as ethylene, propylene and the like in the process of cracking paraffin oils according to the equations: (a)  $C_{10}H_{22} \longrightarrow C_4H_{10} + C_6H_{12}$ ; (b) the formation of an alkylsulfuric acid by treatment with  $H_2SO_4$  (d. 1.8),  $C_6H_{10} + H_2SO_4 \longrightarrow C_6H_{11}(HSO_4)$ , and (c) the hydrolysis of the acid to the corresponding alc.,  $C_6H_{11}(HSO_4) + H_2O \longrightarrow C_6H_{11}OH + H_2SO_4$ . Production on a large scale is carried on by the Standard Oil Co. according to the following flow sheet: (1) removal of  $H_2S$  and moisture by suitable absorbents in towers; (2) conversion to the alkyl sulfate continuously in towers, or by the batch method in large tanks fitted with agitators; (3) settling to remove oils; (4) hydrolysis of acid by mixing it with several vols. of water; (5) distn. of the alcs.; (6) rectification; and (7) reconcn. of the  $H_2SO_4$  from a d. of 1.4 to a d. of 1.8. With regard to the possible future of the process, one refinery



alone produces 12,000,000 cu. ft. of gas daily varying from 10 to 12% in olefin content. Gases from the Burton still are particularly well fitted for treatment. By treating the alkylsulfuric acid with an acetate, acetic esters are formed:  $C_3H_7(HSO_4) + CH_3COONa \rightarrow CH_3COOC_3H_7 + NaHSO_4$ . Propylene with  $H_2SO_4$  gives  $Me_2CHHSO_4$ , which is hydrolyzed to isopropyl alc. and this, either by catalytic oxidation or by dehydrogenation, yields acetone. The refinery gases contain considerable ethylene but its absorption requires high temps. and high concns. of acid while propylene is taken up in the cold in simple absorption towers; consequently at the present time isopropyl alc., which for most technical purposes will serve as well as EtOH, is the chief product of the plant.

H. L. OLIN

Third semi-annual motor gasoline survey. N. A. C. SMITH. U. S. Bur. of Mines. *Repts. of Investigations*, Serial No. 2220, Feb. 1921.—The initial b. p. and the 20% point are lower while the 90% point and the end-point are higher than the year before. The av. b. p. of the present survey is  $263^\circ F.$  compared with  $264^\circ F.$  the year before.

F. W. PADGETT

Tentative specifications for asphalt for use in damp-proofing and waterproofing. ANON. *Proc. Am. Soc. Testing Materials* 20, I, 716-9(1920).—The serial designation is D40-17T. Three classes are distinguished by m. p. and penetration: m. p.  $54.5-60^\circ$ , penetration, 50-75; m. p.  $46-54.5^\circ$ , penetration 75-100; m. p.  $38-46^\circ$ , penetration 100-125. The m. p. is to be taken by the standard ball and ring method, in a water bath. Ductility at  $25^\circ$  on 1 sq. cm., cross section not less than 30 cm.  $D_{25}^{25}$  not greater than 1.08. Bitumen sol. in cold  $CS_2$  not less than 95%. Loss on heating a 50 g. sample at  $163^\circ$  for 5 hrs. not greater than 1%; penetration of the residue not less than 50% of the original sample. Ash, not more than 4%. The d. is detd. by  $H_2O$  displacement; the sample is weighed in a small Pt dish or crucible suspended by a silk thread or fine Pt wire. The soly. is detd. by weighing 1-2 g. in an Erlenmeyer flask, adding 100 cc.  $CS_2$  in small portions with agitation, until all lumps have disappeared, allowing to stand corked for 15 min. and filtering by suction on an asbestos felt in a Gooch crucible. Decantation of the first soln. is stopped at the first appearance of sediment, which is then washed with small portions of  $CS_2$  brought on the felt and finally washed until colorless. Air is drawn through until the odor of  $CS_2$  has almost vanished, the residue is dried at  $105^\circ$  for 30 min. and weighed. If org. material is present in the insol., ignite at red heat, and weigh again. Report % sol. in  $CS_2$ , org. insol., and ash.

M. R. SCHMIDT

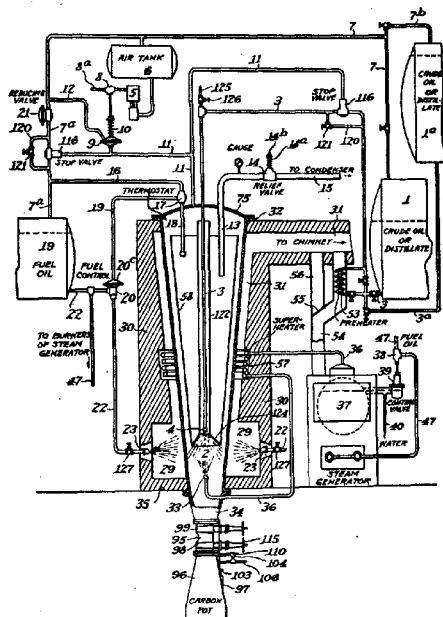
The colloidal mill and its use (BLOCK) 13. Standardized method for the determination of solidification points, especially of naphthalene and paraffin (WILHELM, FINKELSTEIN) 2. Origin of natural fuels (RIGAUD) 8.

Treatment of waste soda liquor obtained in the purification of petroleum. R. NISHIKAWA, T. YAMADA and NIPPON PETROLEUM Co. Japan 35,934, Mar. 9, 1920. The waste soda liquor, containing petroleum, free soda, and petroleum soap, is treated with 1-20% methylated spirit, warmed and set aside; 3 layers are formed. The upper layer contains paraffin, the middle petroleum soap, and the lower soda liquor containing  $Na_2SO_4$ . After recovery of alc., the materials of each layer can be utilized as such.

Liquid asphalt. G. MURAKAMI. Japan 36,321, May 5, 1920. 37.5 kg. asphalt are mixed with 37.5 kg. petroleum pitch with warming, cooled moderately, then with 67 kg. benzine, 14.4 l. portland cement and 28.8 l. lime under agitation.

Cracking petroleum hydrocarbons. C. S. DAVIS. U. S. 1,369,787-8, Mar. 1. Crude petroleum, distillate or residuum to be cracked is fed into a retort 2 through a

spray nozzle 4 under a pressure in excess of that in the retort. Steam may be fed into the retort through an opposed nozzle 33. External burners heat the retort to a cracking temp. The retort is tapered and gases and vapors within it are caused to circulate



by the aspirating action of the nozzles and by an inner shell within the retort. An outlet pipe 23 is so placed within the retort as to draw off a certain portion of the cracked vapors which, are led to a condenser while other heavier vapors may recirculate through the hottest zone of the retort.

## 23—CELLULOSE AND PAPER

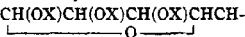
A. D. LITTLE

**Paper pulp supplies from Chile.** ANON. *J. Roy. Soc. Arts*, 68, 769-71(1920).

—There still remains in southern Chile nearly ten million acres of primeval forest containing alerce, coihue, and Chilean pine, all of which are excellent materials for paper making.

H. H. HARRISON

**Constitution of cellulose. I. Acetolysis of ethylcellulose.** KURT HESS AND WALTER WITTELSBACH. *Z. Elektrochem.* 26, 232-51(1920).—It is suggested that the mol. of hydrocellulose, for which the name *celluxose* is suggested, consists of a dextrose or a cellobiose mol. in which the HO groups are etherified by dextrose or cellobiose residues. Of the various possibilities, the formula



(OX)CH<sub>2</sub>OX, in which X represents the radical  $\text{—CHCH(OH)CH(OH)CHCH(OH)—}$

CH<sub>2</sub>OH, is in closest agreement with the proportion of cellobiose acetate (6.2 g.) and penta acetyldextrose (12 g.) obtained from 10 g. cellulose by acetolysis. The dex-  
trins, which are present in the form of acetates when the max. proportion of cellobiose acetate is not reached, are looked upon as mixed partial degradation products of the cellulose mol., resulting from the removal by hydrolysis in a variety of ways of one or more dextrose or cellobiose residues. Expts. on the acetolysis under very mild conditions of ethylcellulose uniformly confirmed the deduction from the above formula that when degradation has proceeded sufficiently far, the ethoxy no. of the ethyldextrin acetates produced should be less than that of the ethyldextrose. This result is not explained by the older formulas. The marked difference between cellulose and its derivs., such as nitrate, acetate and the products obtained by the action of acids, alkalies, or Zn or Cu-NH<sub>4</sub> compds., is accounted for by considering such derivs. to be derived from the above formula, while cellulose consists of a no. of such mols. united through residual affinities of HO groups. The disintegrating effect of the agepts named is due to their competition for these residual valencies. It is also suggested that the physical characteristics of cellulose as a hollow fiber are reproduced in the arrangement of the cellulose mols. in the cellulose complex, and that this complex may be broken down by mechanical means, *e. g.*, in the case of cellulose which has been subjected to prolonged heating or grinding; the product thus obtained represents a stage of disintegration approaching the less profound of those produced chemically. Similar considerations may apply to the mols. of hemicelluloses, protein and rubber.

C. J. WAST

**Wood cellulose.** F. LENZE, B. PLEUS AND J. MÜLLER. *J. prakt. Chem.* 101, 213-65(1921).—Scarcity of cotton in many countries during the war led to wood cellulose as a substitute for a great variety of uses, and it is probable that its use will be continued during peace times. After an extended study the authors have found that by extg. the cell fiber with 17% NaOH and pptg. the dissolved material by means of acids and alc., a method previously used for the detn. of  $\alpha$ -cellulose, various other substances in the fiber can also be detd. These substances comprize oxycellulose, hydrocellulose, cellulose-dextrins, hemicelluloses such as xylan and mannan, pectins, lignin, fats and resins. For a complete removal of these, repeated extns. with alkali are necessary; even then, substances yielding furfural may remain in traces. To ascertain the nature of the hemicelluloses it is necessary to convert them into sugars by boiling the alkali-sol. constituents of the cell fiber for 5 hrs. with 4% HCl, and then identify the resulting carbohydrates. It was found that the constituent of the fiber which yielded furfural on distn. with HCl was a pure xylohemicellulose. Another hemicellulose, mannan, which on hydrolysis with dil. HCl yielded mannose was also present. Oxycellulose can be isolated from the other alkali (17%-sol. constituents of the cell fiber, and detd. quant. by boiling the ppt. obtained by acidifying the alk. soln. with 5% HNO<sub>3</sub>. The product thus obtained is easily sol. in 17% NaOH, and yields on distn. with HCl a methylfurfural which gives an alc.-sol. phloroglucide.

D. BREESH JONES

**Hydration of sulfite and esparto pulps.** *Papeterie* 43, 146-9(1921).—Sulfite, especially when prepd. by cooking at a low temp. with a weak acid, hydrates very readily in the beater, owing to the presence of hemicelluloses. This is very desirable for parchment or grease-proof papers, but must be avoided in the manuf. of print or writing papers. Esparto pulp, being a soda pulp, does not easily hydrate, and may be advantageously mixed with sulfite to reduce the tendency of the latter to hydrate too readily. Moreover, esparto gives suppleness and bulk to the paper and makes

it take the ink particularly well even under moderate pressure, which is especially important for lithographic work.

A. P.-C.

**Electrolytic cells in the paper industry.** ANON. *Papeterie* 43, 149-54 (1921).—Very brief outline of the extent to which electrolytic Cl and NaOH are used in the pulp and paper industry in Europe. Their use in France is not likely to develop at present, as the French market is already overstocked with Cl, and if the pulp and paper mills were to prepare their NaOH electrolytically they would probably experience difficulty in disposing of the excess of Cl thus produced.

A. P.-C.

**Further investigation of materials suggested for the manufacture of paper.** *Bull. Imp. Inst.* 18, 323-35 (1920).—Mature papyrus stems are richer in cellulose and give a higher yield of pulp than the young stems (42 as compared with 34%). The stems could be utilized for the manuf. of wrapping paper but would be unsuitable for white paper. Bourdie grass does not give a sufficiently high yield of pulp to justify the soda process. With lime it gave a brown paper of fair quality, but the pulp did not bleach well. The pulp contained a considerable amt. of pith and the paper is, therefore, harsh. Kokerboom (*Aloe dichotoma*) is not a promising paper-making material, as it gives only a fair yield of pulp of moderate quality, which cannot be bleached. *Hibiscus tiliaceus*, "vau," gives a good yield of inferior pulp. Matai or black pine (*Podocarpus spicatus*) gives a low yield (25%) of pulp, which has good felting qualities but which cannot be satisfactorily bleached. A bamboo, *Tabacca brava*, from Brazil, gives about 48% pulp, which cannot be bleached, however, when prepd. by the soda process, but which bleaches readily when the sulfate process is used. Aninga (*Montrichardia arborescens*) yields a pulp furnishing a good brown paper, but it cannot be bleached.

C. J. WEST

The colloidal mill and its use (BLOCK) 13. X-ray spectrometric investigations on cellulose (HERZOG, et al.) 3. Coloring paper, etc. (U. S. pat. 1,370,070) 25.

**Regeneration of fibers from waste paper.** K. MASUDA. Japan 35,638, Jan. 28, 1920. Waste paper is treated with mineral acid, boiled with aq.  $\text{Na}_2\text{CO}_3$  or NaOH and load oil (castor oil treated with  $\text{H}_2\text{SO}_4$  and neutralized with alk.) and then beaten.

**Glazed paper from waste.** T. FUJII. Japan 35,872. Feb. 21, 1920. Waste papers are painted with 3 special solns. and glazed through hot rollers. (1) 15 borax, 30 shellac and 100  $\text{H}_2\text{O}$ . (2) 20 *Gloiopeltis furcata*, 20 gelatin or glue, 2 millet-jelly, 100  $\text{H}_2\text{O}$ , 1 alum, clay and coloring matter. (3) 5 egg-white, gelatin and 100  $\text{H}_2\text{O}$ .

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

**Some electrical causes of dust explosions.** DAVID J. PIERCE. *J. Elec. West. Ind.* 46, 240-2 (1921).—This report on investigations of grain-dust explosions states that: (1) elec. sparks will ignite grain dust; this will "flash" at  $550^\circ$  and will propagate flame at  $800-900^\circ$ ; (2) the use of elec. light bulbs in dust clouds may result in explosion if broken, or even if they become overheated; (3) static elec. charges may easily cause such explosions. All these causes have been recently detd. and can be taken care of by proper safety measures (illustrd. by diagrams).

F. H. HOTCHKISS

**The invention of friction matches.** T. KELLEN. *Chem.-Ztg.* 45, 205-6, 225-6 (1921).—Historical. It is concluded that no one person can be considered the inventor of matches.

E. H.

Tests of miners' flame safety lamps in gaseous, coal-dust-laden atmospheres (ILSLEY, HOOKER) 1. The sensitiveness of hexanitrobiphenyl to mechanical influences (VAN DUIN) 10.

**Aromatic nitro explosive compounds.** C. M. STINE. U. S. 1,370,067, Mar. 1. A benzoid hydrocarbon with a multicarbon side chain, *e. g.*,  $C_6H_4MeEt$ , is chlorinated to attach Cl to each of the primary and secondary C atoms of the side chain. The Cl deriv. thus formed is then nitrated with  $HNO_3$  and  $H_2SO_4$  and the nitro product so formed is heated with  $H_2O$  under pressure to replace Cl with OH. The aq. soln. is evapd. to drive off  $H_2O$  and HCl and the dinitrophenyl compd. is further nitrated with  $HNO_3$  and  $H_2SO_4$  to substitute a nitrate group for each OH in the side chain. The products thus obtained are powerful explosives. Any of the following compds. may be produced by this method:  $C_6H_3(CH(NO_2)CH_2NO_2)(NO_2)_2$ ;  $C_6H_3CH_3(CH(NO_2)CH_2NO_2)(NO_2)_2$ ;  $C_6H_3CH_2NO_2(CH(NO_2)CH_2NO_2)(NO_2)_2$ ;  $C_6H_3(CH(CH_2NO_2)CH_2NO_2)_2(NO_2)_2$ ;  $C_6H_3OH(CH_2NO_2CH_2NO_2)_2(NO_2)_2$ ;  $C_6H_3(CH_2NO_2CH_2NO_2)_2NO_2$ ;  $C_6H_3CH_3(CH_2NO_2CH_2NO_2)_2(NO_2)_2$ .

**Desensitized nitrostarch explosive.** K. A. GILLESPIE. U. S. 1,370,015, Mar. 1. Nitrostarch in undried condition, desensitized by the presence of  $H_2O$  and an oil such as a heavy petroleum lubricating oil is used in explosives, together with gum arabic. The explosive thus formed is not ignited by the impact of a rifle bullet.

**Explosives.** C. MANUELLI and L. BERNARDINI. Brit. 155,627, June 17, 1917. Chlorates and perchlorates of biguanide and of guanidine are used as, or in explosives or, equivalently, a mixt. of dicyanodiamide with the corresponding salts of  $NH_4$  in the proportion of two molecules to one. The chlorates and perchlorates of biguanide and of guanidine and also the nitrates and sulfates are obtained by heating dicyanodiamide with corresponding  $NH_4$  salts.

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

**Table of coal-tar intermediates used as developers in dyeing and printing.** ANON. *Color Trade J.* 8, 145-6(1921).—In the table, alphabetically arranged according to the com. names of the developers, are given for each item the chem. name, the uses and a statement of whether or not it was made in the U. S. in 1919.

**Oil-soluble dyes and their uses.** HANS WAGNER. *Farben-Ztg.* 26, 1001-2 (1921).—A brief tabulation of the common oil-sol. dyes and a review of their uses. Oil-sol. azo dyes form true solns., while the basic dyes require a small quantity of fatty acid to be present for the formation of salts before they produce the best colored solns.

F. A. WERTZ

**Manufacture of naphthol yellow S (II).** RAFFAELLE SANSONE. *Color Trade J.* 7, 68-72(1921); cf. *C. A.* 14, 2714.—A somewhat detailed discussion of the app., operations, and tests of products, involved in the manuf. of the dye. Suggestions are made as to modes of sepg. and drying the solid product, and a further suggestion is that the dye might well be marketed in compressed tablet form of standard content. The dye might also well be supplied in paste form to near-at-hand consumers.

FREDERICK BEATTIE

**The dye industry.** E. GEAY. *Industrie chimique* 7, 338-9, 378-80, 418-20(1920); 8, 2-4, 42-4, 82-3(1921).—Review of the rise and development of the dye industry in France, Germany, England, the U. S., Switzerland and Italy, and of the effort put forth in these countries during the recent war; together with an analysis of the causes

which enabled Germany to obtain a virtual monopoly, and of the probabilities of other countries competing successfully with it. A.P.-C.

**New colors and sample cards.** PAUL KRAIS. *Z. angew. Chem.* **34**, Aufsatzteil 22-3(1921).—New colors and samples are classified according to Ostwald's method of color analysis. R. E. SABIN

**Bleaching.** JULIUS. *Textile American* **35**, No. 1, 11-5(1921).—Discusses the methods of "boiling out" and bleaching cotton goods. If the "one boil only" method is used, the goods should first be "wet out" and allowed to stand overnight at about 60°. This steeping softens and opens the fibers and acts on the sizing and extraneous matter, giving the alkali a better chance. The addition of 1-2% diastase for while steeping greatly assists the removal of starches by rendering them sol. The goods are then boiled in a soln. containing 3% of the fabric wt. of a mixt. of 60% NaOH and 40% Na<sub>2</sub>CO<sub>3</sub>, for 8-10 hrs. at 45 lbs. pressure. On well boiled out goods, oil and N should be below 0.25-0.5%. The "one-boil" method is not recommended, and where a good bleach is desired the "two-boil" method should be used. In the two-boil method, boil first with lime, wash, sour in H<sub>2</sub>SO<sub>4</sub>, and boil again with NaOH-Na<sub>2</sub>CO<sub>3</sub> mixt. The alkali from boiling out should be thoroughly removed from the goods before bleaching for efficient work. Bleaching is done by Ca(OCl)<sub>2</sub> or a hypochlorite soln. Completely bottomed heavy goods will require not more than 3 g. Cl per l., and light prints only 25-50% of this amt. After bleaching, wash, sour in weak acid and then wash again. CHAS. E. MULLIN

**Antimony mordants.** ELTON R. DARLING. *Textile World* **J.** **59**, 2111(1921).—D. recommends the use of Ca Sb tartrate containing 47% Sb<sub>2</sub>O<sub>3</sub>, all of which is available, to displace tartar emetic, which contains 43% Sb<sub>2</sub>O<sub>3</sub> of which only 37% is available, and neutralizers. (Cf. C. A. **15**, 759.) The Ca compd., unlike the K, is stable in soln., easily prepd. in the plant, and gives a more uniform mordanting. D. claims the H-tartrate compds. formed in use to be the bad feature of K Sb tartrate solns. and that with the Ca Sb tartrate solns. the Ca H tartrate is immediately decompd. to form insol. Ca tartrate, which has no action on Sb tannate. The Ca Sb tartrate may be prepd. as follows: Dissolve 10 lbs. tartaric acid in 100 lbs. H<sub>2</sub>O and add 10 lbs. chalk. To this add a soln. of 22 lbs. fused CaCl<sub>2</sub> and 15 lbs. tartaric acid in 150 lbs. H<sub>2</sub>O. Heat to 40-50° and add 40 lbs. Sb<sub>2</sub>O<sub>3</sub>, boil 10 min. and allow to settle. Decant the clear soln., crystallize by cooling for about 12 hrs. and filter off the crystals for use. The mother liquor may be used again but in the succeeding batch the 22 lbs. CaCl<sub>2</sub> is omitted. The mordanting bath as generally used contains 22 oz. Ca Sb tartrate to 10 gals. H<sub>2</sub>O. CHAS. E. MULLIN

**Influence of moisture on the shade of dyeing.** J. ROUFFIN. *Cotton* **84**, 78(1919).—Dyeings with certain dyes are modified by heat, yellow shades appearing like orange and orange shades more on the scarlet side. On cooling, the original shade returns slowly. When using dyes that are very sensitive to heat, precautions should be taken in "matching off." It is thought that the variation of shade is due to the hygro-metric state of the material. Exptl. results confirm this hypothesis. Also in *Textile World* **59**, 39-41(1921). NATHAN VAN PATTEN

**Holder for samples during exposure.** H. B. GORDON. *Textile World* **J.** **57**, 3781(1920).—Describes the construction of a very simple and convenient lab. app. for testing 21 dyed fabric samples for fastness to ultra-violet light. A single lamp centrally located in the wheel-shaped sample carrier serves as the light source. CHAS. E. MULLIN

**Kier boiling.** JULIUS. *Textile American* **33**, No. 4, 28-30(1920).—Boiling and bleaching should remove or decolorize "all or nearly all of the nitrogenous and ether-sol. substances" from the fiber. The use of enzymes of animal or vegetable origin to

break down this nitrogenous matter is recommended, as this treatment will allow almost complete removal by washing only. By the use of this treatment at about 49° the boiling may be much shortened and much alkali saved. Boiling may be dispensed with in some cases, only the enzyme treatment being used. NaOH, if too concd. in the presence of air and at high temps., will dissolve the cellulose. Pure, clean cotton will lose 8% in wt. if boiled 4 hrs. in 5% NaOH soln.; therefore boiling must not be carried too far. The temp. should never be above 130°, or about 45 lbs. pressure. The liquor must be sufficient to cover the goods and contain not more than 10 g. NaOH per l. The Na boil is shorter than the Ca boil, gives the goods a softer, fuller handle, but they do not hold the white color as long and it is therefore best for dyeing use. Where goods are to be finished white the Ca boil is best and it has less chem. action on the fiber of the ash. For best results the following are recommended: alkali on the wt. of the goods; complete and immediate removal of the lye from the goods after boiling and thorough cold rinsing before drying; and a clean kier. If "boiling has been properly done the goods should be thoroughly absorbent." C. E. M.

**Removing stains from textiles.** ANON. *Textile World J.* 58, 3210(1920).—Materials that are employed and methods of using them are discussed.

CHAS. E. MULLIN

**Waterproofing of textile fabrics.** WILLIAM H. ADAMS. *Textile World J.* 57, 3779-81, 4687-9(1920).—Processes used in manuf. of waterproof, coated and bonded fabrics and imitation leathers by means of tars, asphalts, pitches, waxes, rubber and rubber by-products, mineral greases and oils, paraffin, resins, linseed oil with or without driers, "vulcanized" linseed, rapeseed, corn or cottonseed oils, pyroxylin or cellulose nitrates and acetates, castor oil, camphor, fillers, pigments, oxides of Al, Pb, Zn, Fe and Cr, acetate or basic acetate of Al, cuprammonium or Zn cellulose compds. Mildew-proofing processes using Cu, Pb, Ni, Co, Cr, As, Sb and Hg compds. against mucors are described, also processes using tar, dead wood and creosote oils, anthracene, naphthalene, creolin, etc., against *Pencilium* and *Aspergillus*. The selection of dyes to assist in mildew-proofing fabrics to be water-proofed is discussed.

CHAS. E. MULLIN

**Backfillings for sheets and cambrics.** WILLIAM B. NANSON. *Textile American* 35, No. 2, 11-2(1921).—Discusses the properties of the various constituents of softener and filler formulas, and gives examples of satisfactory formulas. Gum tragacanth is high in albuminoid N which is dangerous when too much is used, as it is liable to develop an acid reaction and discharge the blueing if ultramarine is used. It is a good binder, either alone or mixed with starch, and gives the finished goods a "smooth, tough, leathery feel." "Pearl starch (corn) produces a thicker paste on boiling with H<sub>2</sub>O than any other starch except potato." It is similar to wheat starch as regards binding qualities, but gives a harsher feel. A mixt. of equal parts corn and potato starches gives a "feel" similar to that due to wheat starch. Wheat starch gives a smooth, thick feel and has powerful adhesive qualities. Potato starch forms a semi-transparent paste on boiling with H<sub>2</sub>O by which it is distinguished from the other starches. On account of the difference in gelatinizing temps. when potato starch is boiled with wheat or corn, the potato is overboiled with a loss in value. CHAS. E. MULLIN

**Action of sea water on cotton and other textile fibers.** CHARLES DORRÉ. *Biochem. J.* 14, 709-14(1921).—The destructive action of sea water is due to bacterial growth. This can be prevented by converting the cellulose (in cotton) to the mono-acetate stage. BENJAMIN HARROW

**Study of wool scouring wastes.** ANON. U. S. Bur. Chemistry. *Textile World J.* 58, 261(1920).—Results of grease wool analyses made to det. whether useful sub

stances can be obtained from wool scouring wastes in quantities and at a cost that will be profitable. The bureau is studying uses of the grease in leather dressing, waterproofing, varnish, lanolin, etc., and methods of recovering K, soap greases and fertilizer. Analyses show wide variations in constituents of unscoured wool even of the same grade. Generally lower grade wools contain more K but less grease than finer wools. Water-sol. matter is higher in low than in higher grades. Pulled and washed wools contain little K. All percentages given refer to grease wool. (a) % grease; (b) % water ext. (made after removal of grease; chiefly org. K and N); (c) %  $K_2O$  in water ext.; (d) % N in water ext.; (e) % moisture (low in warm lab.); (f) % ash. *Ohio delaine wool* (7 samples) a 17.77–41.95, b 6.3–17.14, c 1.14–4.73, d 0.3–0.84, e 1.15–4.99, f 8.42–15.05. *Ohio 1/2 blood* (4), a 18.53–27.75, b 10.62–18.58, c 2.06–4.8, d 0.7–0.88, e 1.8–4.11, f 10.82–17.41. *Ohio 1/8 blood* (5), a 9.48–16.3, b 11.67–20.79, c 3.23–5.98, d 0.42–1.03, e 2.97–5.66, f 9.75–35.7. *Ohio 1/4 blood* (2), a 9.79–10.61, b 16.1–18.0, c 3.91–4.87, d 0.77–0.98, e 4.81–4.87, f 9.74–11.36. *Ohio common and braid* (3), a 6.19–6.89, b 16.75–33.0, c 4.3–6.08, d 0.84–1.03, e 3.15–6.39, f 10.92–13.69. *Montana fine* (2), a 12.23–16.13, b 15.02–20.81, c 3.45–6.4, d 0.57–0.6, e 2.49–2.56, f 30.74–31.33. *Montana 1/2 blood* (2), a 10.95–12.55, b 20.98–22.66, c 4.56–5.59, d 0.45–0.73, e 1.74–2.79, f 24.05–28.09. *Montana 1/8 blood* (1), a 10.54, b 33.02, c 9.48, d 1.09, e 4.22, f 19.9. *Texas fine* (3), a 12.70–21.09, b 10.0–11.76, c 2.7–3.45, d 0.28–0.44, e 2.31–5.91, f 19.44–38.13. *Pulled, unwashed* (1 each), *L.A.*, a 10.36, b 4.79, c 0.23, d 0.25, e 3.0, f 5.75. *A.A.*, a 7.59, b 3.24, c 0.19, d 0.17, e 3.92, f 17.91. *A.*, a 17.41, b 2.93, c 0.27, d 0.15, e 3.12, f 4.37. *B.*, a 12.67, b 2.82, c 0.25, d 0.17, e 3.88, f 3.74. *C.*, a 8.75, b 2.36, c 0.14, d 0.14, e 3.76, f 4.12. *Pulled South American* (1 each), *XX*, a 19.44, b 1.78, c 0.08, d 0.16, e 2.86, f 19.82. *X.*, a 11.21, b 4.24, c 0.17, d 0.28, e 4.1, f 10.91. *A.*, a 9.46, b 3.32, c 0.09, d 0.21, e 3.49, f 9.17. *B.*, a 6.23, b 4.45, c 0.71, d 0.31, e 3.77, f 7.67. *C.*, a 5.14, b 5.15, c 0.24, d 0.37, e 3.34, f 5.45. *South American 1/2 blood* (2), a 5.5–6.82, b 8.86–8.94, c 2.43–2.56, d 0.2–0.24, e 2.6–5.05, f 8.98–10.65. *South American 1/8 blood* (1), a 10.38, b 14.38, c 3.73, d 0.44, e 5.21, f 14.27. *Montevideo 1/2 blood* (1), a 13.91, b 22.34, c 5.92, d 0.71, e 4.06, f 15.19. *Montevideo 50s* (1), a 10.39, b 15.68, c 2.99, d 0.38, e 3.59, f 10.62. *Cape, fine* (8), a 12.69–24.37, b 10.4–21.86, c 2.17–4.88, d 0.42–0.82, e 1.94–4.01, f 21.58–35.62. *Australian* (3), a 15.31–17.77, b 9.52–15.86, c 1.97–3.63, d 0.17–0.66, e 2.26–4.79, f 15.3–17.74. *New Zealand 1/2 blood* (1), a 14.41, b 13.64, c 3.6, d 0.49, e 3.52, f 7.59. *New Zealand X-bred* (1), a 9.91, b 12.06, c 3.31, d 0.52, e 4.2, f 9.76.

CHAS E. MULLIN

**War substitutes and their criticisms.** PAUL GALEWSKY. *Z. angew. Chem.* 33, I, 305–6 (1920).—G. discusses artificial leather and silk, their value, and some criticisms of the products. C. J. WEST

**Prevention of stream pollution by dye and intermediate wastes (CASSELMAN) 14.**  
**Textile oils (RASSER) 27.**

BUCHERER, HANS TH.: *Lehrbuch der Farbenchemie*. 2nd Ed. revized. M. 1.20, bound M. 130 + 40% Teuerungszuschlag.

**Natural dyestuffs.** E. HART and I. J. STEWART. *Brit.* 155,726, Feb. 21, 1920. Dyestuffs are extd. from certain Australasian vegetation by treatment with a hot soln. of  $Na_2CO_3$  and  $CaO$ , filtering off the liquid, and if necessary, evapg. it to dryness. The vegetation comprizes *Eucalyptus rostrata*, *E. globulus*, *E. amygdalina*, *E. corymbosa*, *Exocarpu cupressiformis*, *Acacia harpophylla*, *A. polybotrya*, *A. melanoxylon*, *Mallothus discolor*, *Banksia* such as *Banksia marginala*, *Aster argophyllus*, and *Casuarina* including *Casuarina equisetifolia*.



**Sulfide dyestuff from *Andropogon vulgaris*.** S. SARRÒ and M. KUHO. Japan 35,997, Mar. 18, 1920. Alk. ext. of *Andropogon vulgaris*, Hack, or its encrustments is neutralized with mineral acid, from which the dyestuff is pptd., dried and made to paste by adding a small amt. of alkali. 150 g. of the paste are gradually added to a melting mixt. of 160 g.  $\text{Na}_2\text{S}$  and 68 g. S, heated during 5-7 hrs. under agitation and evapd. to dryness. The dyestuff is stable to light, friction and washing.

**Dyeing and finishing cloth.** C. H. CROWELL. U. S. 1,370,412, Mar. 1. Colored paraffin is applied to one side of a woven fabric to impregnate the interwoven threads on that side and color them. U. S., 1,370,413 relates to similar treatment.

**Scouring vegetable fibers.** E. T. J. WATREMEZ. U. S. 1,370,076, Mar. 1. Vegetable fibers are scoured by steeping them in a bath formed of NaOH soln., Javelle water and ZnO and then treated with acid.

**Coloring paper, cloth or similar materials.** R. SYKORA. U. S. 1,370,070, Mar. 1. Indefinite color designs are produced on paper or other fabrics by incorporating  $\text{H}_2\text{O}$  and a dyeing substance into the material and then treating its surface with a dehydrating agent, e. g., Na zincate.

**Waterproof cloth.** Y. HAYASHI. Japan 36,323, May 5, 1920. Hemp or cotton cloth is painted 3 times with soln. (1), then with (2) and (3), the reverse side being painted with (4). (1) is a mixt. of 27 l. sea-water, 3.75 kg. wheat flour, 7.5 kg. chalk, 1.8 kg. fish oil pitch and 180 g. pine resin. (2) is a mixt. of 750 g. *Hydrosme rivieri* powder and 36 l.  $\text{H}_2\text{O}$ . (3) is a mixt. of 1 lb. asphalt, 75 g. fish oil pitch, 0.18 l. petroleum and 0.9 l. gasoline. (4) is a mixt. of 18 l. sea-water, 187.5 g. *Hydrosme rivieri* powder, 1 lb. creosote oil, 1 lb. naphthalene and 75 g. ammonia water.

**Artificial hemp.** Z. NAKAGAMI. Japan 36,315, May 5, 1920. Purified cotton threads are immersed in 5% Na borate soln. for 3 hrs., sepd. from the soln., dried, put in a pasty soln. of *Hydrosme rivieri*, dried, and treated with steam containing  $\text{NH}_3$  for 2-30 min. in a closed vessel.

**Artificial woolen cloth.** K. TAKANI. Japan 36,395, May 18, 1920. The cloth is prepd. by painting soln. I or soln. II 2-3 times on cotton-flannel, the product being waterproof. (I) Mixt. of 37.5 g. India rubber, 1260 cc. gasoline, 180 cc. petroleum, 7.5 g. S and pigment or dyestuff. (II) Mixt. of 37.5 g. India rubber, 1260 cc. gasoline, 180 cc. petroleum, 90 cc. drying oil, 90 cc. lacquer, 7.5 g. S, 75 g. litharge, NaOH and pigment.

**Bulrush fiber.** T. AZUMA. Japan 36,356, May 10, 1920. Bulrush immersed in a warm satd. soln. of soda ash is arranged in a layer on which powdered CaO is spread, another layer of bulrush is arranged over this and then CaO again alternately to a thick layer. After cooling, the fiber is collected and bleached.

**Treatment of wild silk yarn.** S. SAKANÉ. Japan 35,964, Mar. 11, 1920. Wild silk yarn is washed with warm soda soln., soaked for 10 hrs. in 10% HCl, treated for 2 hrs. with 30% soap at 95°, washed with dil.  $\text{H}_2\text{SO}_4$ , then with  $\text{H}_2\text{O}$ , soaked for 2-5 hrs. in mixt. of load oil (castor oil treated with  $\text{H}_2\text{SO}_4$  and neutralized with alkali) and  $\text{H}_2\text{O}$ , dried, steamed for 20 min. and its surfaces are expanded mechanically.

**Threads.** S. KASUYA. Japan 36,336, May 7, 1920. Threads of vegetable origin are immersed in  $\text{H}_2\text{SO}_4$  of 50° Bé. cellulose hydrate being formed, and then in Pb acetate or  $\text{BaCl}_2$  soln. The product is strong and has a good affinity for dyestuffs.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

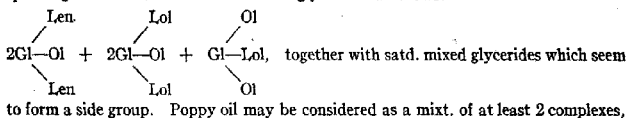
**Lakes and pseudo-lakes and their methods of preparation.** MAURICE DE KESSEL. *Rev. chim. ind.* 29, 237-74, 299-305(1920).—Review of the properties, methods of

prepn. and uses of a large no. of lakes used for pigments. Numerous formulas for their prepn. are given.

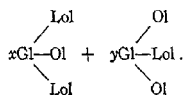
A. P.-C.

**The drying process of fatty oils with respect to their use in trade and the arts.**  
A. EIBNER. *Farben-Ztg.* 26, 823-7, 881-87 (1921).—Extensive tests show that linseed oil films are least likely to crack, and nut oil films are just a trifle better than those of poppy-seed oil which are most likely to crack. The gain in wt. curve for linseed oil films over 60-day periods, rises rapidly to a max. at about the time the films become free from tackiness and then drops to a loss of 17 to 24% of the max. gain. Poppy-seed and nut oil curves rise slowly and not as high as the curve of linseed and finally show a loss of 50 to 100% of the max. gain. Poppy-seed oil has the further undesirable tendency to soften spontaneously with age. The cracking of artists' paints applied in paste form is similar to that of a mud bog. The paste with very fine pigment particles suspended in an oil vehicle constitutes a dispersoid system in which cohesion and adhesion are equalized. Sp. gr. of the pigment surface tension of the oil, size of pigment particle, etc., influence this condition. When the vehicle loses wt. and shrinks through the drying process, the equilibrium of the system is destroyed and cracks develop. This theory was demonstrated by applying a ZnO-poppy-seed oil paste on an undercoat of fairly dry red lead-poppy-seed oil paint. The ZnO showed cracks in a few hrs. A coarser grained ZnO paste did not crack in four years. Similar pastes of fine and coarse-grained vermilion, caput mortum, etc., behaved in the same manner. The optimum grain size for crack formation is about 0.1 $\mu$ ; ultramarine and Prussian blue pigments come within this range. Hence poppy-seed and nut oils should be used in artists' colors only with pigments of suitable grain size. Addition of highly volatile liquids to paste vehicles decreases the tendency to crack formation on account of their low surface tension and resultant ability to hold up the disperse equilibrium. Copaiba balsam, lavender oil, thickened turps, etc., which are slowly volatile, increase the tendency to cracking because they increase the shrinkage of the total vehicle at the time of max. shrinkage of the fatty oil. Addition of wax, paraffin, etc., cannot eliminate the danger of cracking. Undercoats or surfaces to which a paint is applied are classed as neutral or not neutral according to their tendency to cause crack development; to the former belong glass and all other surfaces which exert no influence; to the latter, new wood and other porous surfaces. Positively catalytic surfaces accelerate the drying of paint applied to them. At relatively low temps. a poppy oil film applied to Pb will dry in 48 hrs., lose all its initial gain in wt. in 19 days, and nearly disappear in 60 days. Even olive and almond oil and synthetic triolein will dry on Pb. A paint undercoat contg. pigments which accelerate the drying of oil, if not perfectly hardened, will cause catalytic oxidation of the finishing coat and hasten cracking of the latter. This action results from the diffusion of the catalytic agent. Rapidly drying linseed oil paints serve as much better undercoats than those contg. poppy-seed oil. Tests to det. the safest pigment to use with poppy-seed oil in undercoats gave the following series, in which the last is the most neutral: red lead, white lead, ZnO, lithopone, clay. Poppy-seed oil paints made with ZnO, sienna Co blue, ocher, etc., and applied to poppy seed oil-red lead undercoat that was free from tackiness developed cracks in from 1 to 8 hrs., even before the finishing coat had dried. This is of extreme importance to artists, but the trouble is not likely to occur in commercial painting where linseed oil is used. Sandpapering or rubbing of films increases the life of the finished job in that it permits a firmer bond and reduces the danger of its catalytic drying effect on the succeeding coats. An artist using poppy oil vehicles may overcome its defects by rubbing between coats or by applying all his paints within 4 hrs. before the underlying coats have begun to dry (called "primamal-erie"). Linseed oil films kept in total darkness require up to 64 hrs. to dry and to show a max. gain in wt. In direct sunlight both linseed and poppy oil films dry in a min-

imum time, and then tend to soften and become sticky again. The most recent analyses of linseed oil indicate its compn. to be linolenic acid (Len), 23%; linolic acid (Lol), 26%; oleic acid (Ol), 37%; satd. acids, 8%; glycol (Gl), 5%; unsapon. matter, 1%;—corresponding to a mechanical mixt. of mixed glycerides as follows:



to form a side group. Poppy oil may be considered as a mixt. of at least 2 complexes,



The O absorption of fatty oils whether proceeding according to the peroxide theory of Engler or the absorption of a single atom of O at the double linkage according to Fokin (C. A. 3, 2646), is a complicated colloidal chem. process. The drying of linseed oil is not accompanied by any pronounced polymerization as shown by the very slight change in mol. wt. The yellowing of oil films and white lead paint films is due to free linolenic acids. Films dried in moist air, thus permitting partial sapon., discolor more than those in dry air. The acid no. of an oil film increases with age, and this explains the hard drying of paint films contg. basic pigments which neutralize the slowly drying free fatty acids. The gain in wt. of an oil film in H<sub>2</sub>O-satd. air was very slight and irregular for 8 days, and then rose to 3 times a normal max. gain in 24 days. The prevention of rusting of metals by paint is dependent not only on the selection of inhibitive pigments, but also on the vehicle. Bodied oils and varnishes produce films that are less H<sub>2</sub>O absorbent. The drying of oil films proceeds very rapidly in dry air, but the max. gain in wt. is low because of high compensating losses on oxidation. These losses are due to formation of ozonides of the unsatd. acids which are subsequently broken up by H<sub>2</sub>O into various products dependent on the location of the double linkages (see Harries, C. A. 1, 316). Each mol. of Len, Lol, and Ol may produce one mol. of azelaic acid as well as various aldehydes, malonic acid, etc. That ozonides are actually formed in dry oil films and are subsequently broken up may be demonstrated by shaking linexyn with H<sub>2</sub>O, whereupon the azelaic acid and other derivatives will be found in the ext. The ultimate loss in wt. of linseed oil films is less than that of other drying oils because the peroxide of Len produces volatile derivs. of lowest mol. wt. (propionaldehyde), and because its more rapid drying allows peroxides to be exposed to the action of atm. moisture for a shorter length of time. The so-called linseed oil substitutes consisting of natural and artificial resins in suitable solvents, may be adaptable for special uses, but fall far short of the desirable properties of linseed oil.

F. A. WERTZ

"Decamphorated" (entkämpftes) turpentine. HANS WOLFF, VAN DER KERKHOFF. *Farben-Ztg.* 26, 827-8, 945, 1002-3 (1921).—"Decamphorated," or "regenerated" turpentine is turpentine from which pinene has been removed for the manuf. of synthetic camphor. Its use in paint products, except in admixt. with other solvents, is not advisable. v. d. K. claims that some of these products consisting of limonene, dipentene, etc., have b. p., sp. gr., evapn. rates, and solvent properties comparable to those of turpentine and have already gained a place in the German varnish industry. W. disputes this claim.

F. A. WERTZ

Decahydronaphthalene or dekalin. STANLEY SMITH. *Chem. Trade J.* 67, 253 (1920); *Chem. Age* (London) 3, 283 (1920).—This compd., d. 0.9, is recommended as a turpentine substitute in paints, varnishes, boot polishes, etc. It is rather more efficient

as a solvent than turpentine, and is miscible with the latter in all proportions. A mixt. of 70% of turpentine and 30% of dekalin has the sp. odor of the former, while dekalin itself has a somewhat camphoraceous odor. Evapn. is slower than with turpentine and the comparatively high b. p. of 190° makes it a desirable solvent for high-melting resins, while the flash point of 60° reduces fire risk.

M. R. SCHMIDT

**Accidents and injuries to health in varnish manufacture.** HANS WOLFF. *Farben-Ztg.* 26, 943-4(1921).—Injuries to health by the vapors of varnish solvents are relatively slight. Turpentine is the least harmful; then follow in order, benzine, pine oil and aged turpentines blended with Roumanian benzine and lignite distillates, benzene. Slight poisoning with turpentine usually manifests itself by shortness of breath; with other solvents, by dizziness, nausea, and congestion of blood in the head. In severe cases with benzene, paralysis of the extremities and death have been known to occur. The poisonous properties of chlorinated hydrocarbons are not yet definitely known; they vary greatly and are at least as harmful as benzene. Acetylene tetrachloride is very poisonous. The effect of fumes from gum-melting kettles is comparable to that of the usual varnish solvents. None of these vapors is likely to cause chronic "industrial" diseases. Contact of susceptible persons with the solvents themselves often causes skin irritations, and paraffin oil instead of these, should be used by employees for washing their hands. W. reviews sp. accidents reported in varnish factories. F. A. WERTZ

**Various grinding experiences.** KARI WACHWITZ. *Farben-Ztg.* 26, 944(1921).—General considerations of the dry grinding of paint pigments. F. A. WERTZ

**German fossil resin.** F. W. PATZSCHKE. *Halle. Brennstoff Chem.* 2, 59-60 (1921).—Certain lignites from the Oberlausitz region furnish on extrn. a mixt. of approx. 20% montan wax and 80% fossil resin. The latter has a sapon. no. of 119, softening point of 69° and dropping point of 97.5°. The raw mixt. has an I value of 88.4. Application has been made for patent on a process which produces from it a resin of sapon. no. 260, easily and completely sapond., having a dielec. const. 3.1, and suitable for varnish making. W. B. V.

**German long-needle pine rosin.** F. GOLDSCHMIDT AND G. WEISS. *Z. deut. Oel-Fell-Ind.* 41, 81-2(1921).—Contrary to the general impression that German rosins differ from the imported American and French varieties, G. and W. show that the analytical constns. are identical and that the observed differences must be caused by different conditions during distn. Three samples were analyzed: (1) from Königsberg, dry and brittle; (2) from Feucht, near Nuremberg, Bavaria, contg. much turpentine oil; (3) from the firm of Mann in Halle a/S. Their sapon. nos. were 148.8, 118.3, and 136.1, resp. The samples were extrd. with alc., the alc.soln. was evapd. and then distd. with steam. The residual rosin was then dried and powdered. The analytical results of the dried rosins were:

	1	2	3
Sapon. no.....	180.7	178.2	168.8
Acid no.....	160.0	156.2	...
% unsapon .....	5.6	5.4	5.7
% rosin acids .....	94.5	93.1	95.3

The rosin acids freed from unsapon. matter showed sapon. nos. 188.5, 182.8, and 183.1; and I nos. 152.1, 141.3, 149.5, resp. A larger quantity of No. 3 was distd. by steam and the unsapon. matter isolated. It still contd. 1.1% rosin acids and its hydroxyl value (Normann's method) was found to be 104.2, showing it to contain rosin ales. When the original samples were distd. directly with steam, without preceding alc. extrn., the rosin showed a yield of acids by the stearin method of 73.7, 73.9 and 63.9% against 83.4, 83.6 and 79.2% when extrd. with alc. By distg. 100 g. of sample No. 2 directly with slightly superheated steam, only 33 mg. of rosin acids passed over into the distd. turpentine oil.

P. ESCHER

A brief resumé of writing and printing inks. WALTER E. HADLEY. *Am. Dye-stuff Reporter* 8, II, 20-1, 24-6(1921). E. H.

The manufacture of typewriter colors and ribbons. BRUNO WALTHER. *Chem.-Zig.* 45, 169-71(1921).—A brief review and exposition of the technic of mfg. these products. The processes described are mainly mechanical. J. T. R. ANDREWS

Wash bluing (MAYER) 27. Constituents of resins (ZINKE, DZIMAL) 10.

Treating precipitated titanium hydroxide compounds. TITAN CO. A.-G. Norw. 30,311, Jan. 19, 1920. In the manuf. of white pigments from pptd.  $Ti(OH)_3$  compds., the basic Ti salts are treated with an insol. or difficultly sol. metal compd. which forms two or more compds. by the reaction with the specified substance, of which one is neutral, insol. or difficultly sol., and the other a gas.

Anticorrosive paint. S. MATSUSHITA. Japan 35,962, Mar. 11, 1920. 6.375 kg.  $Na_2CrO_4$ , dissolved in 180 l. hot  $H_2O$ , are boiled with 20.525 kg. kieselsguhr, to which 19.5 kg. white lead are added and boiled for 1 hr., then 1.5 kg. NaOH and boiled for 30 min. The product is washed with  $H_2O$ , dried and mixed with suitable vehicle.

Fireproof paint. F. S. VIVAS. U. S. 1,369,857, Mar. 1. A fire-proofing paint adapted for use on wood or paper is formed of milk 19, Na tungstate 5, borax 10, gum arabic 10, kaolin 20, zinc white 10, Na silicate 10, K silicate 6 and feldspar 10 parts.

Paint vehicle. H. A. GARDNER. U. S. 1,370,106, Mar. 1. A paint vehicle which dries to a firm tough film is formed by polymerizing turpentine or pine oil by heating at 80-160° with 5-7.5% of 92%  $H_2SO_4$ .

Paints and varnishes. M. DARRIN. U. S. 1,370,195, Mar. 1. Linseed oil is used together with a synthetic resin obtained by autoclave treatment of solvent naphtha as a vehicle for varnishes or paints. Volatile solvents may be added.

Removing paint or varnish. D. P. CLEVELAND. U. S. 1,370,188, Mar. 1. Paint and varnish are removed from automobiles or other surfaces by treating them with a hot soln. of NaOH or other solvent applied with a blast of air. Cf. C. A. 15, 182.

Fireproof varnish. F. S. VIVAS. U. S. 1,369,858, Mar. 1. A varnish adapted for fire-proofing is formed of linseed oil 25,  $H_2O$  25, silver litharge 25,  $Pb(OAc)_2$  15, a tungstate 5 and  $H_3BO_3$  5 parts.

## 27—FATS, FATTY OILS AND SOAPS

E. SCHERUBEL

Problems of the Scientific Central Station for Oil and Fat Research. D. HOLDE. *Chem. Umschau Fette Oele Wachse Harze* 28, 41-2(1921).—Purely scientific investigations will be given the same attention as problems of applied chemistry. Among the unsolved problems are: why are the m. ps. of mixed glycerides lower than those of the corresponding mixts. of their triglycerides; explt. proof is needed for Eibner's view that the triglycerides of palmitic and oleic acids are non-drying by themselves though they apparently do not retard the drying of linseed oil, in which they occur as mixed glycerides; the constitution of oils like castor oil is very imperfectly known; the transformation of free fatty acids into glycerides without the use of glycerol; the present nomenclature of oil chemistry needs revision. P. ESCHER

Fat cleavage. HELENE JAPHÉ. *Z. angew. Chem.* 34, Aufsatzteil, 35-7(1921).—Discussion of the various well known processes such as autoclave, Twitchell, fermentative and Krebitz. E. SCHERUBEL

Viscosity of saponifiable oils and fats. W. NORMANN. *Chem. Umschau Fette Oele Wachse Harze* 27, 218-8(1920).—New detns. with Engler's viscosimeter are reported

for the following oils. They were first approx. neutralized by NaOH, bleached with fuller's earth and then filtered, except butterfat, which was simply filtered, and tallow, which was only bleached. The first number after the name of the oil is its acid number, next the number in parentheses is the temp. and the number immediately after that is viscosity in degrees Engler. Linseed 0.55, (21) 7.2, (30) 5.0, (50) 2.9, (70) 2.1, (90) 1.7; rape 0.37, (21) 12.9, (31) 7.7, (50) 4.0, (69) 2.6, (89) 1.9; olive 0.29, (19) 12.9, (30) 8.0, (50) 4.0, (70) 2.5, (80) 1.9; coconut 0.05, (30) 5.6, (50) 3.1, (69) 2.0, (89) 1.6; butterfat 2.1, (34.5) 5.75, (40) 4.6, (50) 3.41, (69) 2.24, (90) 1.7; beef tallow 9.5, (45) 5.35, (58.8) 3.6, (79) 2.36, (88.8) 2.1; hardened rape 0.34, (70) 3.5, (80) 2.9, (91) 2.3; hardened linseed 0.62, (69) 3.5, (79) 2.6, (90) 2.2; olive and hardened linseed mixt. in equal amts., (62) 3.3, (73) 2.7, (90) 2.1. N. concludes that (1) the viscosity increases with increasing mol. wt. if satd. acids alone are present; (2) oils contg. unsatd. fatty acids show decreasing viscosity with rising I no. Hardened oils whose end product is practically pure stearic glyceride (such as from linseed oil) have a tendency to crystallize in storage and to expand thereby with sufficient force occasionally to burst the container. Correction. *Ibid* 28, 32 (1921).—The temp. 90° for butter fat above is 70° by mistake in the original.

P. ESCHER

**Determination of the degree of cleavage.** O. STEINER. Osnabrück. *Z. deut. Öl Fett-Ind.* 41, 65 (1921).—Two methods for factory control and one method for "accurate" detn. of the degree of fat cleavage in the Twitchell process are given. Factory control: (1) Gravimetric: 2 g. of the product (freed from glycerol water) are titrated cold in alc. soln. against 0.5N alkali and phenolphthalein until the rose color persists for 2 min. The no. of cc. required  $\times 100 \times$  the figure in the first column of the table corresponding to the oil used gives the %. (2) Volumetric: the same procedure is used as in (1) but 2 cc. is measured in place of weighing 2 g. and the second column is used. When a mixt. of several oils are used, the divisor is found by multiplying the figures in the table by the % of each oil:

TABLE FOR FACTORY CONTROL.

	2 g.	2 cc.		2 g.	2 cc.
Linseed oil.....	14.2	13	Olive oil.....	13.9	12.7
Sesame oil.....	14.25	13.1	Palm kernel oil.....	18.0	17.0
Cottonseed oil.....	14.6	13	Coconut oil.....	18.9	16.9
Corn oil.....	14.1	13	Palm oil.....	14.7	12.8
Peanut oil.....	14.4	13.1	Tallows.....	14.5	12.9
Japan. fish oil.....	13.2	12.5	Rape oil.....	14.0	12.7
Bean oil.....	14.39	12.9			

(3) For more accurate detn. about 2 g. are weighed with approx. accuracy and titrated as before against 0.5N alkali; then enough 0.5N alkali is added to bring its total up to 25 cc.; the whole is boiled for 15 min. and titrated back against 0.5 N acid to obtain the sapon. no. The % of cleavage is then calcd. to the basis of finished product by the formula:  $(100 \times \text{cc. required for neutralizing the free acid}) / \text{cc. required for sapon.}$

P. ESCHER

**Evaluation of technical fats and oils.** K. BRAUN. Berlin-Wilmersdorf. *Z. deut. Öl Fett-Ind.* 41, 82-3 (1921).—Definitions are given for the com. expressions (1) % saponifiable; (2) % separable fatty acid; (3) % separable fatty acids utilized by the soap maker. No. 1 is detd. by the acid no., the sapon. no. and the neutralization no. of the pure fatty acids and represents the sum of the free fatty acids plus the neutral fat. No. 2 is detd. by saponifying the fat, decomp. by HCl and shaking out with ether; No. 3 is detd. as No. 2, using gasoline in place of ether, thus eliminating the hydroxy acids which in the factory remain in the lye. In all cases the unsapon. matter must be

detd. and subtracted. All calcs. are based on the fundamental equation:  $(\text{XCOO})_2 \cdot \text{C}_8\text{H}_8 + 3\text{H}_2\text{O} = 3\text{XCOOH} + \text{C}_8\text{H}_8(\text{OH})_3$ . Example. A fat shows the following data: acid no. 40, sapon. no. 190, ester no. 150 (190-40), sapon. no. of the pure fatty acids 198, mean mol. wt. of fatty acids 282. Then  $\text{KOH} (56): \text{fatty acids} (282): \text{acid no. 40}: \text{X} = 20.14\%$  free fatty acids. Three  $\text{KOH} (56): 3 \text{ fatty acids} + \text{C}_8\text{H}_8 (884): \text{ester no. (150)}: \text{X} = 78.92\%$  of neutral fat.  $\text{KOH} (56): \text{fatty acids} (282): \text{ester no. (150)}: \text{X} = 75.53\%$  of fatty acids combined in the neutral fat. The final calcn. follows: No. 1, the % saponifiable matter, equals 20.14 (free acids) + 78.92 (neutral fat) = 99.06%. No. 2, the % separable fatty acid equals 20.14 (free acids) + 75.53 (combined acids) = 95.67%. No. 3, the separable fatty acid utilized by the soap maker, equal No. 2 less % hydroxy acids. P. ESCHER

**Degree of fat cleavage.** W. FAHRION. *Chem. Umschau Fette Oele Wachse Harze* 28, 36-7(1921).—While J. Davidsohn det. the degree of cleavage in the Twitchell process by saponifying the finished product, liberating and neutralizing the fatty acids and calcg. the % cleavage according to the formula  $100 \times \text{acid no.}/\text{neutralization no.}$ , thus basing percentage on the finished product, W. Fahrion bases it upon the wt. of the original fat according to the formula  $100 \times \text{acid no.}/\text{sapon. no. of fat}$ . P. E.

**An oleaginous Acanthus from Belgian Congo.** J. PIERAERTS. *Bull. sci. pharmacol.* 27, 517-21(1920).—A description, record of wt., dimensions and chem. analysis of *Gilletiella congolana*. Hulls, kernels and oil are analyzed as well as the press-cake. One notable point is the presence of some 47% of crude fatty materials in the kernel. F. S. HAMMETT

**Determination of hydroxy acids in "sulfur olive oils."** F. GOLDSCHMIDT AND G. WEISS. *Z. deut. Oel Fett-Ind.* 40, 649(1920).—According to Stadlinger (C. A. 14, 8164) there is as much as 9% difference in hydroxy acids found in "sulfur olive oil" (obtained from the residue of olive pulp by extrn. with  $\text{CS}_2$ ), depending upon whether petroleum ether b. 70° or unfractionated benzine is used for pptn. G. and W.'s expts. show that the b. p. of the petroleum ether makes no difference in the hydroxy acid content of "sulfur olive oils." E. SCHERUREL

**Textile oils.** E. O. RASSER. *Z. deut. Oel Fett-Ind.* 40, 662-4(1920).—The following characteristics are demanded of a textile oil: (1) High fat content, shown by the detn. of fatty acids, unsapon. matter, neutral fat and free fatty acids. (2) Ready emulsification. Mixts. of fatty oils with mineral oils saponify readily with  $\text{H}_2\text{O}$  when they contain alc.; also many ready-made emulsions are on the market; fatty acids and saponifiable fats emulsify with soda. (3) Absence of autoxidation (cause of spontaneous combustion), shown by the I no., flash point, burning point, volatility at 100° and behavior in Machey's oil-tester (heating to 100° for 1 hr.). The latter has shown 92° to 96° after 1 hr. for 8 olein samples, although their max. temps. ranged from 105.5° to 308° before they finally fell to 92-95°. Olive oil and oleic acid are safe but cottonseed fatty acids are not; plant fibers burn more readily than animal fibers, but coarseness, dyes, moisture content, impurities and storage conditions have an influence. (4) Must not stiffen rapidly at low temp. (5) Freedom from acidity, to prevent corrosion of metals and hardening of leather; acidity can be corrected by adding  $\text{NH}_4\text{Cl}$  or  $\text{Na}_2\text{CO}_3$ . (6) Ready sapon. in order to be easily washed from the fiber. Fatty acids saponify readily, oleic acid at room temp.; neutral fats must be removed by soap; small amts. of mineral oil wash out, larger amts. require soap and considerable time, metal soaps cause spots in washing or dyeing. High temp. during dressing causes the oils to penetrate the fiber and if it is mineral oil it takes colors slowly. Addition of mineral oils is largely a matter of cost; their flash-point should be above 200°. Caragheen may be present as a thickening agent. Olive oil or a good olein is best for dressing; soap,  $\text{NH}_4\text{OH}$  or alkali carbonate for washing. Standardizing is much needed. P. ESCHER

**Wash blueing.** H. MAYER. *Seifensieder Ztg.* 48, 89, 111-2, 129-30, 151-2 (1921).—M. describes briefly the manuf. of 4 types of ultramarine and gives 3 physical tests regarding quality: (1) *Purity of shade* is detd. by spreading a small quantity on white paper, smoothing its surface and comparing its color with a standard grade. (2) *Coloring capacity* is detd. by mixing the sample with 5-10 times its wt. of plaster of Paris and comparing the resulting color with standards. (3) For detg. *fineness*, a quantity is shaken up in H<sub>2</sub>O and the time required for complete subsidence is noted. The general character of rival products may be detd. by boiling the powder sample with 5 times its wt. of H<sub>2</sub>O; starch is shown by the thickening of the soln.; dextrin is recognized by its odor; by adding HCl to the soln. a greenish blue color shows indigo-carmin; absence of color indicates Prussian blue. Several tests for the recognition of aniline dyes are given. The prepn. of ultramarine substitutes is described in more or less detail. Ultramarine blueing is sold in various solid pasty or liquid forms, all of which are discussed. The liquid form is represented by a H<sub>2</sub>SO<sub>4</sub> soln. of indigo, the prepn. of which, as well as that of indigo-carmin, is described in detail. Aniline dyes are now much used but careful selection is necessary; wash blue, China blue, water blue, indigotin, etc., are mentioned as suitable for blueing. P. ESCHER

**Glycerol.** F. C. C. ROBB. *Pharm. J.* 106, 256(1921).—A brief account of the history and technical prepn. of pure glycerol. S. WALDBOTT

**Determination of the purity of spermaceti.** P. BOHRISCH AND F. KÜRSCHNER. *Pharm. Zentralhalle* 61, 703-10, 719-26, 733-7(1920).—Widespread adulteration of spermaceti necessitated the detn. of the consts. of the pure wax in order that closer limits may be set. The sp. gr. was found to be 0.916-0.942 instead of the values usually accepted, 0.890-0.960, and the m. p. 44.0-47.5° instead of 45-54°. Rancidity is caused by exposure to light but not to air. Adulteration with tallow and stearic acid cannot be detected by means of the "grease-spot" test. Paraffin is best detected by warming 0.25 g. spermaceti with 5 cc. 10% alc. KOH and adding 2-3 cc. distd. H<sub>2</sub>O. A cloudiness results if as little as 1% of paraffin is present. Stearic acid is best detected by the method of G. Frerich (cf. *C. A.* 11, 1250). The acid and sapon. nos. are most easily detd. by dissolving 3 g. spermaceti in 20 cc. petroleum ether to which 5 cc. abs. alc. are added. Titration with alc. KOH to a red color with phenolphthalein gives the acid no. Then 25 cc. 0.5*N* alc. KOH are added and after 24 hrs. the excess alkali is titrated. The acid no. should be below 2.0 and the sapon. no. between 118 and 135. The I no. should be 3.06 to 5.0. H. A. SHONLS

**Wool scouring wastes (ANON.)** 25. Apparatus for regenerating waste nickel catalyzer (Jap. pat. 36,355) 18. Effecting chemical reactions (Brit. pat. 155,776) 13.

**Renewing the activity of catalyzers employed for hardening fats.** C. AND G. MÜLLER, SPEISEFETTFABRIK AKT.-GES. Ger. 319,332, Dec. 15, 1918. The catalyzer, after mechanical sepn. from the hard fat, is stirred with a well refined oil for some time with heating and then sepd. from the oil mechanically and by washing with a fat solvent. In certain circumstances this treatment may be followed by a treatment with H. E. g., olive oil was reduced with H for 3.5 hrs. in the presence of a catalyzer obtained by heating Ni borate in a current of H to about 450°. A hard fat was obtained—m. 49.0° (I no. 30.7). After being used repeatedly the catalyzer became practically inactive. The catalyzer was then stirred thoroughly with well refined olive oil for 45 min., with heating, sepd. from the oil and boiled for some time with ether. It was then heated with H for 45 min. at 430-40°. After treatment of the same oil, for 3.5 hrs. in the presence of 2% of the renewed catalyst, a fat was obtained, m. 52.2° (I no. 10.6).



**Apparatus for extracting oil.** N. YAMAMOTO, E. MORIMOTO and M. MORIYAMA. Japan 36,328, May 7, 1920. The extn. tower has a perforated false bottom, under which filtering materials are put and over it the sample. Solvent is dropped from the upper part, while hot air is injected from the bottom. These towers are connected in parallel with cooling and collecting vessels, etc.

**Apparatus for bleaching oils by sunlight.** M. TANAKA. Japan 36,129, Apr. 8, 1920. On an inclined app. extremely thin layers of oil are flowed.

**Scouring compositions.** H. T. БУННЕ АКТ.-ГЕС. Brit. 155,595, Dec. 20, 1920. A solvent of fat for mixing with H<sub>2</sub>O to scour textiles or leather consists of a hydrocarbon or deriv. to which is added 1-5% of fatty acid and sufficient alc. and potash or other alkali lye in equal vols. to produce a clear liquid. It is miscible with H<sub>2</sub>O in all proportions. In an example, 20 g. colza oil acid are stirred into 1000 g. benzine and 8 g. caustic potash of 50° Bé. and 8 cc. alc. are added.

**Soaps; fatty acids.** W. J. MÖLLERSH-JACKSON. Brit. 155,866, July 25, 1919. Soap powders are produced from drying oils, train oils, and other oils and fats forming soft or unstable soaps by concentrating the soda soaps, mixed or not with alkali carbonate, at 180-300° and a corresponding pressure of about 15 atm. Polymerization of the unsatd. fatty acids takes place, and coloring and malodorous bodies are driven off.

## 28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

**The history of sugar.** BARTHOLOMEW VIOLA. *Louisiana Planter* 65, 379-81, 398-9(1920).—A sketch giving the history of sugar from 900 B. C. to 1850 A. D.

C. H. CHRISTMAN

**Fructose.** A. DANIEL. *Chem.-Ztg.* 45, 4-5(1921).—D. points out the following advantages of fructose as a foodstuff over sucrose. Fructose is resorbed directly and assimilated to a larger extent than sucrose. Fructose is oxidized much more quickly than either cane sugar or dextrose, and in larger amts. in equal time intervals. The abundant formation of CO<sub>2</sub> is important in the treatment of tuberculosis and other affections. Fructose also effects a saving in fats and protein. It can be readily manufd. in sugar factories from chicory roots, which give good yields per acre. The exhausted chips and the leaves may be used for feeding purposes. The bitter taste of the fresh leaves can be remedied by drying and mixing with other feeds. The molasses may be converted into coffee substitutes and into dyestuffs. (Cf. C. A. 15, 188.)

F. W. ZERBAN

**Analyses of refined sugars.** FREDERICK J. BATES, *et al.* *Intern. Sugar J.* 22, 654-5(1920).—220 samples, representing 40 grades, were analyzed, by the Bates polariscope for sucrose, Ost's copper carbonate liquor for reducing sugars, the sulfated ash method for mineral impurities, and vacuum drying at 70° for moisture. Most of the samples were found to be remarkably pure, whether of beet or cane origin. The av. sucrose was 99.95, the rest consisting of very small amts. of reducing sugars, and traces of ash and moisture. The beet sugars averaged a trifle higher in polarization than the cane sugars, probably owing to traces of raffinose. The H-ion concn. of twice normal solns. of the sugars was also detd. by the use of Clark and Lubbs' indicators, and the acidity or alkalinity was detd. with 0.1 N HCl, NaOH and Ba(OH)<sub>2</sub>. The cane sugars were almost always acid, and beet sugars sometimes so. No relation whatever was found to exist between the H-ion concn. and the titrated acidity. Screen tests disclosed extreme variations in mechanical compn. of samples sold as the same grade. In the candy test on beet sugars the hydrolysis reached less than 1%, while in cane sugars it was as high as 15%.

F. W. ZERBAN

**The Queensland government central sugar mills.** W. J. SHORT. *Intern. Sugar J.* 23, 86-9(1921).—Report for 1919-20. Two tables are given, showing in detail cost of manuf., and chem. control results. The total sugar production was again short, owing to drouth. Some improvements have been made in mechanical equipment, and the Thomas and Petree process (*C. A.* 12, 1131) is now used in all the mills but one, with satisfactory results.  
F. W. ZERBAN

**The sugar industry in Mauritius.** H. A. TEMPANY. *Intern. Sugar J.* 23, 81-6 (1921).—This is the report of the Dept. of Agriculture for 1919. The total sugar production reached 235,490 tons, or 10.56% of the wt. of cane ground. 94.45% of the total production was high-grade white sugar. Fertilization with  $(\text{NH}_4)_2\text{SO}_4$  and with  $\text{NaNO}_3$  has given increased yields, but no decided results were obtained with K or P. The molasses produced is largely used as a fertilizer, and the remainder distd.  
F. W. ZERBAN

**The cost of production of sugar in Java.** H. C. PRINSEN-GEERLIGS. *Intern. Sugar J.* 23, 78-9(1921); cf. *C. A.* 14, 2869.  
F. W. ZERBAN

**The Antigua central sugar factory.** FRANCIS WATTS. *West Indian Bull.* 18, No. 3; *Intern. Sugar J.* 23, 132-9(1921).—"A survey of fifteen yrs. of work."  
F. W. ZERBAN

**The Australian sugar industry.** T. D. CHATAWAY. *Intern. Sugar J.* 23, 140-6 (1921).—An article dealing with the general and economic phases of the industry.  
F. W. ZERBAN

**Report on sugar manufacture and by-product utilization in Hawaii, 1920.** ANDREW ADAMS, et al. *Intern. Sugar J.* 23, 155-7(1921); cf. *C. A.* 14, 651.—Further improvement in the refining quality of Hawaiian sugars is necessary, as they contain too much ash and invert sugar. This may be accomplished by more efficient clarification and by improving on the working of low grades. More pans and crystallizers will have to be used. The type and size of crystallizers are of importance, and data on this subject are being collected. With the ever increasing extn. there has lately developed a tendency of the sirups to have a lower purity than the clarified juices, and unusually high undetd. losses have been observed. This is probably due to certain dextrorotatory gums which cause a higher polarization in the juice; upon evapn. these gums are coagulated and a drop in purity results. This difficulty may be obviated by improved methods of clarification.  
F. W. ZERBAN

**Experience gained during the 1917-18 and 1918-19 campaigns.** FRANZ F. KNOR. *Listy Cukrovd.* 38, 377-9(1920).—Analytical and factory data of the Dobrovice refinery are tabulated (cf. also *C. A.* 15, 956). During the unfavorable 1918-19 campaign the difference between the direct polarization of the raw juices and the actual sugar content detd. according to Clerget equalled, on an av., 0.9%, indicating the presence of considerable quantities of dextro-rotatory nonsugars. This partially explains the low yields obtained during the campaign.  
JOHN M. KRNO

**Cane mill efficiencies.** T. WISHART. *Intern. Sugar J.* 22, 625-9(1920).—W. calls attention to the fact that the usual mill reports give only a vague idea of the actual performance of a milling plant, and proposes a number of formulas leading to figures which actually express the efficiency of the plant, considering the material handled per unit wt. of machinery, per unit dimensions of rolls, per horse power, and also the quality of crushing and the extn. For details the original should be consulted.  
F. W. ZERBAN

**The cost of concentrating light juice.** JÁN POKORNÝ. *Z. Zuckerind. Tschoslov. Rep.* 44, 339-42(1920).—P. shows, giving actual cost figures, that the cost involved in concg. light juice in a well constructed evaporator system is extremely low and there-

fore consideration of the proposed method of concg. by fractional freezing is out of the question.

JOHN M. KERNO

The entrainment of juice during evaporation and boiling as the cause of high "unknown losses" of sugar. ANON. *Intern. Sugar J.* 23, 95-7(1921).—This is a résumé of articles by Schweizer, Van Ham, Olsen, and de Haan, previously noted (*C. A.* 14, 858, 2274, 2427).

F. W. ZERBAN

The settling of precipitates in general and of cane juice precipitates in particular. NOEL DEER. *Intern. Sugar J.* 22, 618-24(1920).—The problem studied is a special case of the phenomena governed by Stokes' law. In this particular instance the concn. of the suspensions was variable, and where cane juice was used, also the previous treatment of the juice. Expts. with  $\text{Al}(\text{OH})_3$  suspensions in water, in a glass tube 1450 mm. high and 19.3 mm. wide, showed that with very dil. suspensions, up to 0.08 g.  $\text{Al}_2\text{O}_3$  per 100 cc., the quantity of material settled in unit time is proportional to the concn. of the suspension. With concns. of 0.08 to 1 g. per 100 cc. the particles in their downward path interfere with each other and the rate of fall is controlled by the concn. of the suspension. With still higher concns. there is no more free fall, but rather a shrinkage of a column under its own wt. In a further study of the case of medium concn. it was found that during the first min. or so no settling could be observed, the suspension behaving like a colloidal soln. After that the formation of 5 distinct zones is observed, the 1st, upper, zone being clear, the 2nd zone containing stragglers, a 3rd, small, zone with the particles practically at rest, a 4th zone with the particles in a strong gyrotory, and at the same time a downward and upward motion, and a 5th zone of settled material, shrinking at a slow rate. After a certain time zones 3 and 4 disappear and the upper level of zone 5 becomes sharp and flat. This position is termed the "critical position"; the period of settling before the critical position is reached is called "phase of free fall," and the one after that "phase of restricted fall" (cf. *C. A.* 10, 1152). If  $h$  is the total height of the column, and  $d$  the height of zone 5 at the critical position, then  $d/h$  is const., and also  $(h-d)/t$ , where  $t$  is the time to the critical position. By varying the concn. of the suspension of  $\text{Al}(\text{OH})_3$  from 0.0888 to 0.4340 g. per 100 cc., it was found that (1) the rate of settling decreases as the concn. of the suspension increases; (2) the quantity of material in g. which falls the unit distance in the unit of time, up to the critical position increases regularly with the initial concn. of the suspension up to 0.2 g. per 100 cc., after which it remains const. up to at least 0.45 g. per 100 cc.; (3) the mean concn. at the critical position increases with the initial concn. of the suspension. After the critical position is reached, the rate of settling decreases with each increment of time, approx. according to the formula  $(1/t) \times \log [(h_0 - h_n)/(h_t - h_n)] = \text{const.}$ , where  $t$  is the time,  $h_0$  the height of the column at the critical position,  $h_t$  that after time interval  $t$ , and  $h_n$  that after the settling has practically stopped. Next, expts. were made with cane juice the natural acidity of which was 1.75 cc.  $N$  per 100 cc., with phenolphthalein, and which was limed with 0.5, 0.75, 1, 1.25, 1.5, 1.75, and 2 cc.  $N$   $\text{CaO}$  suspension per 100 cc. It was then boiled and poured into a settling tube surrounded by steam at  $100^\circ$ . The juices limed with 0.5 and 0.75 cc. were found to be underlimed, the one with 1 cc. doubtful, and those with 1.75 and 2 cc. overlimed. The one with 1.5 cc. was representative of good practice, and here the ppt. settled 7 cm. per min. The critical position is at 0.75 of the height of the column, and the ultimate vol. of the ppt. is 15% of the total. There is practically no difference in the rate of settling for juices of 15 and of  $20^\circ$  Brix. Some further tests on the effect of the initial height of the column upon the final rate of settling after the critical position showed that the taller column settled faster. Tall settling tanks are, therefore, preferable, the vols. being equal.

F. W. ZERBAN

The elimination of filter presses in raw-sugar factories. STUART M. LITTLEMORE. *Chem. Eng. Mining Rev.* 13, 109-11(1920).—The Thomas and Petree process of clarifica-

tion (C. A. 12, 1131) is now in use at 14 sugar factories in Australia and has given complete satisfaction. Where triple crushing is employed, the process is worked as follows: The juice from the second mill is defecated with lime, settled, and decanted, yielding mud and juice. The latter is mixed with the first mill juice and the mixt. defecated and settled separately; the mud joins the second mill juice prior to defecation and settling. The defecated and decanted mixed juice goes to the evaporators. Both muds are returned to the mill and distributed over the bagasse between the first and second mills. Maceration water is applied after the second crushing, and the third mill juice is pumped back on the bagasse from the first mill. All the mud finally goes to the furnaces, together with the final bagasse. There is no ill effect on the extn. or on the burning quality of the bagasse. The process obviates losses due to fermentation and yields a sugar of higher polarization than the processes used previously. F. W. ZERBAN

Suggestions on the production of a better raw sugar. S. S. PECK. *Intern. Sugar J.* 23, 158-61 (1921).—An improvement in the refining quality of raw sugars may be attained in 2 ways, either by manuf. a sugar of higher polarization, or else by better clarification. The use of finer-mesh screen for straining the raw juice will help in this direction, as it will remove more bagacillo. The latter contains gums and coloring matters which are partly dissolved during clarification as carried out at present. The gums increase the viscosity of the products and render filtration, boiling, and curing difficult, and affect the filtering quality of the affination sirup in the refinery. The use of  $H_2PO_4$  on second-mill juices has given good results, notably decreasing the quantity of suspended matter, organic, ash, and gums. The use of Filter-Cel, as proposed by Zerban (C. A. 14, 2686) appears promising for the same purpose. F. W. ZERBAN

Chemistry of clarification in plantation white sugar manufacture. J. P. OONVIG. *J. Soc. Chem. Ind.* 40, 22-4R (1921).—A description of the various methods used in tropical white sugar manuf. is given, and a discussion of the colloid-chem. conception of cane-juice clarification presented (cf. C. A. 11, 303, 716; 13, 1027, 1263; 14, 2868). F. W. ZERBAN

The comparative values of decolorizing carbons. F. E. THOMAS. *Intern. Sugar J.* 23, 162-5 (1921).—In comparing the color of a raw sugar soln. with that of the same soln. after decolorization, it is usually impossible to make both readings in a cell of the same size; thus a serious error is introduced from the beginning. But even granting that correct results are obtained here, the efficiency of a carbon should not be based on the comparative decolorizing effect of equal wts. of different carbons, but rather on the relative quantities of different carbons required to effect the same decolorization. The question of cost of manuf. has also been overlooked so far. It is easy enough to increase the amt. of active C in a carbon, but this gives less carbon and largely increases its cost. The following standard method of the evaluation of carbons is proposed. Norit is to be used as a standard, because it is uniform in decolorizing power and readily obtainable everywhere. The carbons to be compared should be used as delivered by their makers. The raw sugar should be of not too low a grade and just on the acid side. It should be dissolved to 50° Brix. The soln. obtained after treatment with 5% Norit is used as the standard of comparison. Then the amt. of the carbon under examn. is detd., which gives the same decolorization as the 5% of Norit. If necessary, comparisons may be made with 2.5 and 7.5% Norit. The carbons should be added in the cold, brought to the boil in equal intervals of time, and filtered, the first half of the filtrate being returned to the original soln. and filtered again to eliminate the fine particles which nearly always come through at the beginning. F. W. ZERBAN

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Purifying liquids (Brit. pat. 155,611) 13.

REDLICH, FELIX AND ZIEGLER, STEGMUND: *Die Zukunft der Cechoslovakischen Zuckerindustrie*. Brünn: Published by the authors. 1919.

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White sugar. S. TANAKA. Japan 36,289, May 3, 1920. Crude sugar soln. is mixed with 1-2.5% milk of lime, neutralized with  $H_3PO_4$  or its acidic salts until a slightly alk. reaction is obtained, heated at 90-95°, filtered, cooled below 60°, neutralized with  $SO_2$  to phenolphthalein, filtered, bleached with 0.05%  $SO_2$  and crystd. by the usual method.

Palatable sirup from sugar beets. S. F. SHERWOOD. U. S. 1,370,372, Mar. 1. An edible sirup is prepd. by heating sugar beets in  $H_2O$  (preferably to a temp. of about 80°), sepg. the liquid and heating it in an autoclave to a temp. of about 109° for about 1 hr. and blowing off steam from the autoclave at about 15-min. intervals during the heating to eliminate substances of objectionable flavor.

## 29—LEATHER AND GLUE

ALLEN ROGERS

The theory of leather formation. X. W. FAHRION. *Collegium* 1920, 125-8; cf. *C. A.* **13**, 522.—Polemical reply to an article by Moeller (*C. A.* **14**, 2999).

I. D. G.

The relation between hydrolysis and adsorption. W. MOELLER. Hamburg. *Collegium* 1920, 109-25, 152-66, 209-23, 267-77 (1920).—The expts. were carried out with hide powder such as is used in tannin detns. In the preliminary discussion M. points out that protein gels swell in distd. water alone. This is due to the hydrolysis which begins as soon as the protein is dead, since repeated extrn. will dissolve all of it. This same process must also be going on during adsorption expts. and accounts for the difference in the results of such expts. with boneblack and with hide powder. The only equil. seems to be that between the unchanged hide and its hydrolysis products. The sample (4.4 g.) of hide powder was the same in all expts. With distd. water alone 1.7% was found to dissolve at the end of 1 hr., 24 hrs., and 3 days; in 8 days this had become 2.44% and in 30 days it was still the same. At the latter time about 50% of the dissolved matter was colloidal as indicated by a kaolin filtration. The change in acidity was followed by titration with the use of both phenolphthalein and methyl orange as indicators. Similar expts. were carried out with hide powder and each of the following:  $HCl$ ,  $HCl$  and  $NaCl$ ,  $AcOH$ , glycine, and then glycine together with each of these acid combinations. The results are collected in 29 tables and 23 charts and are discussed theoretically. M. concludes that: (1) The first action of acid on hide powder is hydrolytic. (2) The hydrolysis with inorg. acids is both more rapid and greater than with org. (3) The hydrolysis is apparently checked in the first 24 hrs. by the presence of neutral salts, but begins very suddenly after that time. (4) Besides the hydrolysis process there is also adsorption between the non-hydrolyzed protein and the products of hydrolysis combined and uncombined with acid ions, ionized protein mols., and unionized protein mols. (5) The swelling is due to the adsorption of

hydrated protein ions by the unchanged hide fibers. (6) The hydrated hydrolyzed proteins are dehydrated by the addition of neutral salts and consequently no swelling can take place as a result of the adsorption. (7) With amphoteric substances (glycine) there is no hydrolysis and so no swelling. (8) The apparent acidity obtained with different indicators after the acid has acted on the hide for an hour differs considerably from the true acidity due to the so-called protein error (Eiweissfehler) and gives no true idea of the course of the reaction. (9) Very different results may be expected with gelatin owing to the structural and chem. difference between the gelatin and the hide powder. *Ibid* 319-31, 382-7.—A series of expts. with 0.1 *N*, 0.5 *N* and *N* NaOH and with Ca(OH)<sub>2</sub> similar to the previous series with acids was carried out. The results are brought together in 11 tables and 8 charts. In all cases the adsorption increased with both the concn. and the time, which with NaOH was extended to 8 days and with Ca(OH)<sub>2</sub> to 30 days. M. concludes that the action of acids and alkalis on proteins is often parallel with the adsorption of dyes and tanning materials but is very different in nature and furnishes no support for a theory as to the latter. The dyes and tanning substances are either neutral or so weakly acid that hydrolysis is excluded.

I. D. GARARD

**The acid titration of chrome liquors.** A. W. THOMAS AND S. B. FOSTER. *J. Am. Leather Chem. Assoc.* 16, 61-3(1921); cf. *C. A.* 14, 2102; 15, 609.—The official method for titrating chrome liquors can be made to yield more accurate results by the addition of about 50 g. NaCl to the soln. before titration is commenced. I. D. G.

**The swelling of hides.** G. GRASSER. *Collegium* 1920, 405-16, 456-64, 512-20.—The author reviews the work of other workers on the swelling of hides after soaking in acid and in salt solns. He then outlines his own expts., from which he concludes: The various org. acids have the same effect upon the swelling of hides as has HCl. The max. of swelling is reached after several hrs., but the concns. of the acids in the different maxima differ. Monochloroacetic acid causes the max. swelling in the lowest concn. It is followed by oxalic acid, then by lactic acid, formic acid, and acetic acid. Max. of swelling as to time was first reached through oxalic acid, then lactic acid, acetic acid, monochloroacetic acid, and formic acid. In terms of rate of swelling, the order was as follows: Monochloroacetic acid, lactic acid oxalic acid, acetic acid. With regard to their respective dissociation consts., the order of the five acids was as follows: Monochloroacetic acid, formic, lactic, oxalic, acetic, and there seems to be no correlation between these and any of the swelling factors above mentioned. The effect of salts on the swelling of hides needs further investigation. However, the author brings out the following: The sulfates cause a rapid and profound swelling; the effect of the nitrates is more gradual, but is greater in the high concns. The neutral salts act very gradually and cause a medium swelling, resembling in this case the chlorides. In the case of the salts, neither their concns. nor their dissociation consts. seem to show any proportional relation to the rate of hide swelling. Addition of sugar to various salt or acid solns. had no effect upon the swelling of the hide, proving that the phenomenon of swelling is independent of the osmotic pressure of the soln.

B. S. LEVINE

**Notes on the one-bath chrome tanning process and on the determination of the tanning intensity by the agglutination method.** E. STIASNY. *Collegium* 1920, 479-85.—An unfavorable criticism of the work of E. Griliches (cf. *C. A.* 14, 3819). B. S. L.

**Behavior and determination of free sulfuric acid in leather.** II. W. MORLER. *Collegium* 1920, 465-70.—A further criticism of Immerheiser's method for the detn. of free H<sub>2</sub>SO<sub>4</sub> in leather and for the study of its behavior. Argumentative proof is offered of the inadaptability of this method for the detn. of free H<sub>2</sub>SO<sub>4</sub> in leather. The outstanding point of the author is that during the process of evapn. on the sand bath the free acid of the leather combines with the chlorides, forming double salts and

thus cannot be accounted for as free  $\text{H}_2\text{SO}_4$ . The free acid also acts upon the org. constituents of the ext., especially upon the phenols, and in the process of evapn. destroys them, undergoing destruction itself, and thereby becoming unaccountable as free  $\text{H}_2\text{SO}_4$ .

B. S. LEVINE

Notes on the work of Baldracco and Camillo on the shake and filter method. R. LAUFFMANN. *Collegium* 1920, 430-1; cf. C. A. 14, 1460.—L. states that the conclusions of B. and C. that the filter method gives lower results in non-tans than does the shake method is based upon reactions which could be equally regarded as indication of the possibility that the shake method does not completely retain the tannins. He further states that the modifications introduced by B. and C. are not new and have been fully described by Th. Veit in *Collegium*, 1908, 216-24, 235-8 and that they do not all constitute an important improvement in the procedure.

B. S. LEVINE

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War substitutes (artificial leather, etc.) (GALEWSKY) 25.

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**Making leather.** O. RÖHM. Brit. 156,079, Oct. 12, 1920. The patent relates to processes for the unhairing, neutralization, and bating of hides and skins by means of pancreatic enzymes after a short preliminary treatment with an alk. soln., and consists adding in a salt of an alkali or alk. earth to the alk. soln. in order to obviate stiffness and over-plumping. The alk. soln. may contain caustic alkalies, alk. earths, or  $\text{NH}_3$ , the salts of alkalies to be added thereto comprizing  $\text{Na}_2\text{SO}_4$  or  $\text{K}_2\text{SO}_4$  or chlorides of Na, K, Ca, Ba, etc. After the preliminary treatment, in order to neutralize the caustic alkali,  $\text{NaHCO}_3$  or other suitable agent such as  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{Cl}$ , etc., or weak acids such as boric acid or lactic acid, may be added together with the pancreatic enzymes. The preliminary treatment with, e. g.,  $\text{NaOH}$  and  $\text{Na}_2\text{SO}_4$  may be intensified to effect unhairing before treatment with enzymes. The mixt. of  $\text{NaOH}$  and  $\text{Na}_2\text{SO}_4$  may be used as a bath or by painting it on to the flesh side. Preferably the alkalies and alkali salts are mixed together in the solid state, being fused and allowed to set in the form of small tablets, plates, etc. The enzyme liquor remaining after unhairing or bating may be used again for the preliminary soaking of hides, etc. A suitable bating liquor for use after unhairing with  $\text{CaO}$  comprizes 100 l. of  $\text{H}_2\text{O}$ , 100 g. of pancreas ext., 150 g. of  $(\text{NH}_4)_2\text{SO}_4$  and 250 g. of  $\text{Na}_2\text{SO}_4$ .

**Tanning.** C. F. L. BARBER. Brit. 155,887, Sept. 16, 1919. A chromé tanning-liquor is prepd. by the action of synthetic tans upon a soln. of chromic acid or a dichromate and acid soln. In an example, a one-bath liquor is prepd. by dissolving 100 lbs. of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 20 gal. of boiling  $\text{H}_2\text{O}$ , adding thereto 100 lbs. of strong  $\text{H}_2\text{SO}_4$ , and while it is still at the b. p. further adding 220 lbs. of a synthetic tan prepd. by sulfonating a phenol, condensing this product with an addition of  $\text{HCHO}$ , and afterwards neutralizing with  $\text{NaOH}$  or  $\text{KOH}$ . In a two-bath process, the hide is first drummed in a chromic acid or acidulated dichromate soln., and then in a strong synthetic tan soln. Cf. 16,647, 1886, and 287, 1908.

